

Byzantievite, $\text{Ba}_5(\text{Ca}, \text{REE}, \text{Y})_{22}(\text{Ti}, \text{Nb})_{18}(\text{SiO}_4)_4[(\text{PO}_4), (\text{SiO}_4)]_4(\text{BO}_3)_9\text{O}_{21}[(\text{OH}), \text{F}]_{43}(\text{H}_2\text{O})_{1.5}$: the crystal structure and crystal chemistry of the only known mineral with the oxyanions (BO_3) , (SiO_4) and (PO_4)

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ABSTRACT

The crystal structure of byzantievite, $\text{Ba}_5(\text{Ca}, \text{REE}, \text{Y})_{22}(\text{Ti}, \text{Nb})_{18}(\text{SiO}_4)_4[(\text{PO}_4), (\text{SiO}_4)]_4(\text{BO}_3)_9\text{O}_{21}[(\text{OH}), \text{F}]_{43}(\text{H}_2\text{O})_{1.5}$, a new mineral from the moraine of the Dara-i-Pioz glacier, the Alai mountain ridge, Tien-Shan Mountains, northern Tajikistan, was solved by direct methods and refined to $R_1 = 13.14\%$ based on 3794 observed $[F_o > 4\sigma|F|]$ unique reflections measured with Mo- $K\alpha$ X-radiation on a Bruker P4 diffractometer equipped with a CCD detector. Byzantievite is hexagonal, space group $R\bar{3}$, $a = 9.1202(2)$ Å, $c = 102.145(5)$ Å, $V = 7358.0(5)$ Å³, $Z = 3$, $D_{\text{calc}} = 4.151$ g cm⁻³. The empirical formula (electron microprobe analysis) is $\text{Ba}_{5.05}[(\text{Ca}_{8.99}\text{Sr}_{0.96}\text{Fe}_{0.42}^{2+}\text{Na}_{0.20})_{\Sigma 10.57}(\text{Ce}_{3.46}\text{La}_{1.54}\text{Nd}_{1.20}\text{Pr}_{0.30}\text{Sm}_{0.26}\text{Dy}_{0.41}\text{Gd}_{0.32}\text{Th}_{0.39}\text{U}_{0.17}^{4+})_{\Sigma 8.05}\text{Y}_{3.53}]_{\Sigma 22.15}(\text{Ti}_{12.31}\text{Nb}_{5.30})_{\Sigma 17.61}(\text{SiO}_4)_{4.65}(\text{PO}_4)_{3.12}(\text{BO}_3)_{8.89}\text{O}_{22.16}(\text{OH})_{38.21}\text{F}_{4.89}(\text{H}_2\text{O})_{1.5}$, $Z = 3$, calculated on the basis of 124.5 (O + F) a.p.f.u. The H₂O and OH contents were calculated from structure refinement (F + OH = 43 a.p.f.u.; H₂O = 1.5 a.p.f.u.), and B was determined by SIMS. The crystal structure is a framework of Ti-Ba-Ca-REE-dominant polyhedra and SiO₄, PO₄ and BO₃ groups. In the crystal structure, there are 50 cation sites, 23 of which are fully occupied and 27 partly occupied: six of the 27 partly-occupied sites are >50% occupied, 21 <50% occupied. The crystal structure of byzantievite is an intercalation of three components, one fully ordered with 100% occupancy of cation sites, and two partly ordered with cation-site occupancies of 67% and 17% respectively. Byzantievite is the only known mineral that contains all three of the oxyanions (BO₃), (SiO₄) and (PO₄) as essential components.

KEYWORDS: byzantievite, new mineral, borate-silicate-phosphate, electron microprobe analysis, crystal structure, short-range order, Dara-i-Pioz massif, Tajikistan.

Introduction

BYZANTIEVITE occurs in the moraine of the Dara-i-Pioz glacier, the Alai mountain ridge, Tien-Shan Mountains, northern Tajikistan, in association with quartz, microcline, aegirine, titanite, still-

wellite-(Ce), danburite, zircon, astrophyllite, thorite and calybeborosilite (Pautov *et al.*, 2010). Byzantievite, ideally $\text{Ba}_5(\text{Ca}, \text{REE}, \text{Y})_{22}(\text{Ti}, \text{Nb})_{18}(\text{SiO}_4)_4[(\text{PO}_4), (\text{SiO}_4)]_4(\text{BO}_3)_9\text{O}_{21}[(\text{OH}), \text{F}]_{43}(\text{H}_2\text{O})_{1.5}$, is the only known mineral which contains all three of the oxyanions (BO₃), (SiO₄) and (PO₄) as essential components. Byzantievite is a mineral of extreme chemical and structural complexity, and it has no natural or synthetic analogues. To acknowledge the complexity and beauty of the structure of this

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mineral, we chose the name byzantievite (Pautov, pers. comm.). Here, we report on the crystal structure and crystal chemistry of byzantievite.

Experimental details

Sample description

The single crystal of byzantievite that was used in this work is a translucent brownish-yellow grain with dimensions $0.056\text{ mm} \times 0.08\text{ mm} \times 0.12\text{ mm}$. This crystal gave the best diffraction pattern of the five crystals examined. Diffraction patterns of all five crystals have numerous continuous streaks. We suspected that the presence of Th and U caused partial metamictization but attempts to anneal a crystal resulted in loss of periodicity.

Electron microprobe analysis

We used another crystal from the same sample for the electron microprobe analysis. That crystal was

analysed with a Cameca SX100 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 kV, a probe current of 10 nA, a final beam diameter of 10 μm , and count times on peak and background of 20 and 30 s for major and minor ($<1\text{ wt.}\%$) elements, respectively. A total of 20 elements were sought and the following X-ray lines and standards were used: F- $K\alpha$, fluorophlogopite; Na- $K\alpha$, albite; Si- $K\alpha$ and Ca- $K\alpha$, diopside; P- $K\alpha$, apatite; Ti- $K\alpha$, titanite; Fe- $K\alpha$, fayalite; Y- $L\alpha$, YAG; Nb- $L\alpha$, $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$; Ba- $L\alpha$, baryte; La- $L\alpha$, LaPO_4 ; Ce- $L\beta$, CePO_4 ; Pr- $L\beta$, PrPO_4 ; Nd- $L\beta$, NdPO_4 ; Sm- $L\beta$, SmPO_4 ; Gd- $L\beta$, GdPO_4 ; Dy- $L\beta$, DyPO_4 ; Th- $M\alpha$, ThO_2 ; U- $M\beta$, UO_2 . Data were reduced using the PAP procedure of Pouchou and Pichoir (1985). The chemical composition of byzantievite is given in Table 1 and is the mean of 10 determinations; B_2O_3 was determined by SIMS (Pautov *et al.*, 2010). The empirical formula is $\text{Ba}_{5.05}[(\text{Ca}_{8.99}\text{Sr}_{0.96}\text{Fe}_{0.42}\text{Na}_{0.20})_{\Sigma 10.57}$

TABLE 1. Chemical composition (wt.%) and unit formula (a.p.f.u.) for byzantievite.

Oxide	Wt.%	Unit formula			
P_2O_5	3.58	Ti	12.31	M^{2+}, M^+	
Nb_2O_5	11.38	Nb	5.30	Fe^{2+}	0.42
SiO_2	4.52	ΣD	17.61	Ca	8.99
TiO_2	15.90			Sr	0.96
ThO_2	1.65	B	8.89	Na	0.20
UO_2	0.74	Si	4.65	$\Sigma(M^{2+}, M^+)$	10.57
B_2O_3^*	5.00	P	3.12		
Y_2O_3	6.44			M^{3+}, M^{4+}	
La_2O_3	4.06	Ba	5.05	La	1.54
Ce_2O_3	9.17	ΣA	5.05	Ce	3.46
Pr_2O_3	0.79			Pr	0.30
Nd_2O_3	3.26	OH**	38.21	Nd	1.20
Sm_2O_3	0.73	H_2O^{**}	1.5	Sm	0.26
Gd_2O_3	0.93	F	4.89	Gd	0.32
Dy_2O_3	1.22			Dy	0.41
FeO	0.49			Th	0.39
CaO	8.15			U^{4+}	0.17
SrO	1.61			$\Sigma(M^{3+}, M^{4+})$	8.05
BaO	12.51				
Na_2O	0.10			Y	3.53
H_2O^{**}	6.00				
F	1.50			ΣM_{all}	22.15
Sub total	99.73				
Less O $\equiv$ F	0.63				
Total	99.10				

* determined by SIMS.

**calculated from structure solution and refinement.

(Ce_{3.46}La_{1.54}Nd_{1.20}Pr_{0.30}Sm_{0.26}Dy_{0.41}Gd_{0.32}Th_{0.39}U_{0.17})_{Σ8.05}Y_{3.53}]_{Σ22.15}(Ti_{12.31}Nb_{5.30})_{Σ17.61}Si_{4.65}P_{3.12}B_{8.89}O_{119.62}H_{41.21}F_{4.89} = Ba_{5.05}[(Ca_{8.99}Sr_{0.96}Fe_{0.42}Na_{0.20})_{Σ10.57}(Ce_{3.46}La_{1.54}Nd_{1.20}Pr_{0.30}Sm_{0.26}Dy_{0.41}Gd_{0.32}Th_{0.39}U_{0.17})_{Σ8.05}Y_{3.53}]_{Σ22.15}(Ti_{12.31}Nb_{5.30})_{Σ17.61}(SiO₄)_{4.65}(PO₄)_{3.12}(BO₃)_{8.89}O_{22.16}(OH)_{38.21}F_{4.89}(H₂O)_{1.5}, $Z = 3$, calculated on the basis of 124.5 (O + F) a.p.f.u. (atoms per formula unit). The H₂O and OH contents were calculated from structure refinement (F + OH = 43 a.p.f.u.; H₂O = 1.5 a.p.f.u.). The simplified formula is Ba₅(Ca, REE, Y)₂₂(Ti, Nb)₁₈(SiO₄)₄[(PO₄), (SiO₄)]₄(BO₃)₉O₂₁[(OH), F]₄₃(H₂O)_{1.5}, $Z = 3$ (with regard to O_{22.16} and O₂₁ a.p.f.u. in empirical and simplified formulae, see section on Chemical formula).

Data collection and crystal-structure refinement

A single crystal of byzantievite was mounted on a Bruker P4 automated four-circle diffractometer equipped with graphite-monochromated Mo- $K\alpha$ X-radiation and a CCD 4K APEX detector. The intensities of 23045 reflections with $-12 < h < 12$, $-12 < k < 12$, $-134 < l < 143$ were collected to

60.00°2 θ using 30 s per 0.1° frame, and an empirical absorption correction (SADABS, Sheldrick, 1998) was applied. The refined unit-cell parameters for the rhombohedral cell in the hexagonal setting (Table 2) were obtained from 7521 reflections with $I > 10\sigma I$. The crystal structure of byzantievite was solved by direct methods with the Bruker SHELXTL Version 5.1 system of programs (Sheldrick, 1997) and refined in space group $R\bar{3}$ to $R_1 = 13.14\%$ and a GoF of 1.519. Our attempts to solve the structure in space groups of higher symmetry, $R\bar{3}$, $R3m$, $R3c$ and $R32$ were unsuccessful. In particular, we could not complete the coordination polyhedra for most cations. Below, we will show that the crystal structure is characterized by local pseudo-mirror planes m_z which eliminate an inversion centre. Refinement of the structure was extremely difficult because of the profound disorder of cations and anions (27 out of 50 cation sites are partly occupied). We used the following strategy: (1) an initial set of atom positions was derived by direct methods; (2) missing atoms were located from difference-Fourier maps to get reasonable crystal-chemical atomic arrangements for specific parts of the structure; (3) site occupancies for cation sites

TABLE 2. Data collection and structure-refinement details for byzantievite.

a (Å)	9.1202(2)
c (Å)	102.145(5)
γ (°)	120
V (Å ³)	7358.0(5)
Space group	$R\bar{3}$
Z	3
Absorption coefficient (mm ⁻¹)	7.13
$F(000)$	8487
$D_{\text{calc.}}$ (g cm ⁻³)	4.151
Crystal size (mm)	0.056 × 0.08 × 0.12
Radiation/filter	Mo- $K\alpha$ /graphite
Upper 2 θ -value for structure refinement (°)	45.00
$R(\text{int})$ (%)	10.88
Reflections collected	23045
Independent reflections	4296
$F_o > 4\sigma[F]$	3794
Refinement method	Full-matrix least squares on F^2 , fixed weights proportional to $1/\sigma F_o^2$
Goodness of fit on F^2	1.519
Final $R_{(\text{obs.})}$ (%)	13.14
$[F_o > 4\sigma[F]]$	$R_1 = 14.28$
R indices (all data) (%)	$wR_2 = 37.61$

TABLE 3. Atom coordinates and isotropic-displacement factors ($\text{\AA}^2$) for byzantievite.

Atom	Site occ. (%)	x	y	z	U_{iso}^*	Atom	Site occ. (%)	x	y	z	U_{iso}^*
D(1)	100	0.8947(6)	0.5614(6)	0.98244(6)	0.0261(14)	O(7)	100	0.8117(19)	0.883(3)	0.0399(2)	0.02
D(2)	100	0	0	0.97553(3)	0.0149(19)	O(8)	100	0.5157(15)	0.1848(16)	0.1043(2)	0.02
D(3)	100	0	0	0.35890(7)	0.0103(18)	O(9)	100	0.953(2)	0.628(2)	0.9640(3)	0.02
D(4)	100	0	0	0.2562(3)	0.0123(18)	O(10)	100	0.669(3)	0.046(2)	0.0383(3)	0.02
D(5)	100	0	0	0.30898(3)	0.0120(18)	O(11)	100	0.529(2)	0.741(2)	0.0409(3)	0.02
D(6)	100	0.8981(5)	0.5659(6)	0.01880(2)	0.0160(12)	O(12)	100	0.847(3)	0.329(3)	0.0222(3)	0.02
D(7)	69	0.3348(10)	0.3320(11)	0.85877(8)	0.040(4)	O(13)	100	0.7055(7)	0.1836(9)	0.65222(12)	0.02
D(8)	69	0.9986(9)	0.6664(10)	0.80872(8)	0.050(4)	O(14)	100	0.1893(7)	0.1500(18)	0.98535(10)	0.02
D(9)	17	0.1019(6)	0.0933(4)	0.18471(2)	0.009(6)	O(15)	100	0.145(3)	0.619(3)	0.0162(2)	0.02
D(10)	17	0.5668(15)	0.3279(16)	0.18534(2)	0.004(5)	O(16)	100	0.860(2)	0.529(3)	0.00050(4)	0.02
D(11)	17	0.3337(16)	0.5702(16)	0.18499(8)	0.003(5)	O(17)	100	0.1989(7)	0.146(2)	0.01582(10)	0.02
D(12)	17	0.10241(16)	0.0938(2)	0.14928(2)	0.028(10)	O(18)	100	0.8551(17)	0.331(3)	0.97710(4)	0.02
D(13)	17	0.5543(17)	0.3281(18)	0.14908(2)	0.032(11)	O(19)	100	0.655(3)	0.063(3)	0.91673(14)	0.02
D(14)	17	0.3222(12)	0.5323(12)	0.15006(2)	0.057(14)	O(20)	100	0.931(3)	0.598(3)	0.08500(12)	0.02
M(1)	100	0	0	0.06042(5)	0.0232(14)	O(21)	100	0.5103(19)	0.983(3)	0.9389(2)	0.02
M(2)	100	0.6655(5)	0.6320(5)	0.08415(4)	0.0304(10)	O(22)	100	0.8373(17)	0.144(2)	0.0650(2)	0.02
M(3)	100	0	0	0.39375(6)	0.0119(14)	O(23)	100	0.1584(5)	0.8236(6)	0.0708(2)	0.02
M(4)	100	0	0	0.94121(5)	0.0149(12)	O(24)	100	0.669(3)	0.8426(19)	0.9355(3)	0.02
M(5)	100	0.6667(5)	0.5789(4)	0.04567(4)	0.0257(10)	O(25)	100	0.296(3)	0.1668(18)	0.9375(2)	0.02
M(6)	100	0.9122(4)	0.3332(4)	0.95584(2)	0.0138(9)	O(26)	100	0.5078(9)	0.989(2)	0.06369(16)	0.02
M(7)	100	0.3682(6)	0.0322(6)	0.91743(5)	0.0339(11)	O(27)	33	0.965(5)	0.027(4)	0.25346(10)	0.02
M(8)	100	0	0	0.27458(6)	0.0156(13)	O(28)	100	1.002(9)	0.944(7)	0.4160(2)	0.02
M(9)	55	0.9984(8)	0.6633(8)	0.10806(6)	0.0324(10)	O(29)	100	0.1736(15)	1.013(3)	0.4354(2)	0.02
M(10)	55	0.3382(9)	0.3364(9)	0.89368(7)	0.0324(10)	O(30)	100	0.9864(8)	0.1562(7)	0.23292(15)	0.02
M(11A)	17	0.2488(16)	0.9141(16)	0.87987(14)	0.0324(10)	O(31)	100	0.8590(9)	0.8631(13)	0.56455(15)	0.02
M(11B)	17	0.3266(17)	0.0890(17)	0.87886(15)	0.0324(10)	F(1)	100	0	0	0.7171(3)	0.007(7)
M(11C)	17	0.419(2)	0.990(2)	0.8794(2)	0.0324(10)	F(2)	100	0	0	0.6180(3)	0.013(7)
M(12A)	17	0.671(2)	0.751(2)	0.12276(18)	0.0324(10)						
M(12B)	17	0.4212(19)	0.002(2)	0.12184(17)	0.0324(10)						
M(12C)	17	0.3308(16)	0.0900(17)	0.12261(14)	0.0324(10)						
Si(1)	100	0	0	0.09745(2)	0.042(3)	O(32)	67	0.1398(9)	0.1302(18)	0.18759(17)	0.02
Si(2)	100	0	0	0.90406(2)	0.042(3)	O(33)	67	0.5190(4)	0.3361(12)	0.1823(4)	0.02
Si(3)	100	0	0	0.23833(5)	0.042(3)	O(34)	67	0.2909(15)	0.5005(6)	0.1835(4)	0.02
Si(4)	100	0	0	0.43087(15)	0.042(3)	O(35)	67	0.467(4)	0.534(2)	0.20374(0)	0.02
						O(36)	67	0.316(4)	0.184(3)	0.1272(2)	0.02
						O(37)	67	0.462(4)	0.522(3)	0.1293(2)	0.02
						O(38)	67	0.6510(11)	0.1785(7)	0.1520(3)	0.02

<i>T</i> (1)	63	0.9889(3)	0.6554(2)	0.07080(7)	0.022(4)	O(39)	67	0.329(4)	0.186(2)	0.20653(0)	0.02
<i>T</i> (2)	63	0.6635(12)	0.0060(13)	0.93081(10)	0.009(4)	O(40)	67	0.8547(4)	0.0034(11)	0.15212(16)	0.02
						O(41)	67	0.143(2)	0.299(4)	0.20370(0)	0.02
B(1)	100	0.6695(15)	0.8968(15)	0.0394(5)	0.03	O(42)	67	0.175(3)	0.333(4)	0.1257(2)	0.02
B(2)	100	0.1062(14)	0.7737(15)	0.9632(4)	0.03	O(43)	67	0.4008(6)	0.5633(7)	0.1493(3)	0.02
B(3)	100	0	0	0.7692(6)	0.03	O(44)	33	0.5084(18)	0.317(3)	0.1855(9)	0.02
B(4)	100	0	0	0.5594(5)	0.03	O(45)	33	0.3233(17)	0.5400(18)	0.1474(7)	0.02
B(5)	16.7	0	0	0.48424(15)	0.03	O(46)	33	0.1429(4)	0.1623(3)	0.1503(5)	0.02
B(6)	16.7	0	0	0.14939(10)	0.03	O(47)	17	0.3685(13)	0.5199(9)	0.16858(8)	0.02
B(7)	16.7	0	0	0.81612(11)	0.03	O(48)	17	0.495(7)	0.318(15)	0.1660(2)	0.02
B(8)	16.7	0	0	0.5181(2)	0.03	O(49)	33	0.552(2)	0.373(10)	0.1471(8)	0.02
B(9)	16.7	0	0	0.18175(5)	0.03	O(50)	17	0.132(5)	0.119(9)	0.16727(4)	0.02
B(10)	16.7	0	0	0.84736(17)	0.03	O(51)	17	0.3341(17)	0.5703(9)	0.20605(12)	0.02
						O(52)	17	0.56530(9)	0.3292(2)	0.20560(2)	0.02
						O(53)	17	0.0999(16)	0.095(2)	0.20626(10)	0.02
A(1)	100	0.0718(2)	0.3330(3)	0.00070(3)	0.0213(6)	O(54)	17	0.3248(19)	0.5335(9)	0.13048(2)	0.02
A(2A)	22	0.4115(13)	0.0762(14)	0.83387(10)	0.0202(15)	O(55)	17	0.55690(9)	0.3217(2)	0.12805(2)	0.02
A(2B)	22	0.2719(13)	0.9939(13)	0.83386(10)	0.0202(15)	O(56)	17	0.10573(15)	0.0962(2)	0.12971(2)	0.02
A(2C)	22	0.3329(13)	0.9353(13)	0.83408(11)	0.0202(15)	O(57)	17	0.147(2)	0.3035(13)	0.1889(5)	0.02
						O(58)	17	0.491(3)	0.509(6)	0.1878(15)	0.02
O(1)	100	0	0	0.08206(2)	0.02	O(59)	17	0.306(2)	0.111(7)	0.1878(12)	0.02
O(2)	100	0.1757(11)	0.040(3)	0.1045(2)	0.02	O(60)	17	0.151(7)	0.325(6)	0.1442(10)	0.02
O(3)	100	0	0	0.91972(2)	0.02	O(61)	17	0.519(2)	0.511(3)	0.1485(13)	0.02
O(4)	100	0.1616(11)	0.004(2)	0.89763(18)	0.02	O(62)	17	0.3408(4)	0.163(3)	0.1458(4)	0.02
O(5)	100	0.260(2)	0.786(3)	0.9607(2)	0.02	O(63)	33	0.371(3)	0.523(4)	0.1856(8)	0.02
O(6)	100	0.120(3)	0.929(2)	0.9612(2)	0.02	O(64)	33	0.1414(17)	0.1692(15)	0.1833(7)	0.02

* U_{eq} for 40 atoms listed in Table 4.

were refined, adjusted in accord with the chemical analysis and mean bond lengths, and then fixed; (4) matching site occupancies were assigned to the anion sites that are ligands of those cations; (5) after assembling all parts of the structure, site occupancies for cation and anion sites were fixed and an overall refinement of the structure was done with a limited set of 3794 unique observed reflections ($F_o > 4\sigma F$) with $-9 < h < 9$, $-9 < k < 9$, $-109 < l < 109$, $2\theta \leq 44.98^\circ$. There are three main groups of cations in the structure, with 100%, ~67% and ~17% occupancy, respectively. These cation groups define three components, one fully ordered with full occupancy of cation sites, and two partly ordered with cation-site occupancies of ~67% and ~17% respectively (see discussion below). For the component with 17% occupancy of the cation sites, we were unable to locate all anions. Using a reduced final set of 3794 reflections helped to reduce background noise and improved refinement of the positional parameters of the major cations. The most intense peak in the final difference-Fourier map is $3.69 \text{ e}/\text{\AA}^3$. Scattering curves for neutral atoms were taken from the International Tables for X-ray Crystallography (1992). Site occupancies for the D (= Ti,Nb), M , T and A sites were refined with the scattering curves of Nb, Ce, P and Ba respectively. The site occupancies for the $\text{Si}(1-4)$ sites and $\text{B}(1-4)$ sites refined to integers, indicating that these sites are fully occupied. In accord with the topology of the structure, site occupancies for the $D(9-14)$ and $\text{B}(5-10)$ sites were fixed at about 1/6 (see structure description below). Where $\text{Si}-\text{O}$, $\text{B}-\text{O}$, $T-\text{O}$ and $D(9-14)-\text{O}$ bond lengths were either too short or too long, they were fixed at reasonable values during the refinement. These constrained distances can be detected in the corresponding table as they have an estimated standard deviation of $\leq 0.01 \text{ \AA}$ (non-constrained distances have higher estimated standard deviations).

Details of the data collection and structure refinement are given in Table 2, final atom parameters and site occupancies (%) are given in Table 3, anisotropic displacement parameters for 40 atoms in Table 4, selected interatomic distances in Table 5, refined site-scattering values, assigned populations, incident bond-valence values and total aggregate charges for cation sites in Table 6, and assigned populations, incident bond-valence values and total aggregate charges for anion sites in Table 7. A list of observed and calculated structure factors has been deposited with the Principal Editor of

Mineralogical Magazine and is available from www.minersoc.org/pages/e_journals/dep_mat_mm.html.

Assignment of cation site-populations

Tetrahedral Si and T sites

Six sites are tetrahedrally coordinated by O atoms. The chemical analysis gives $\text{Si}_{4.65}$ and $\text{P}_{3.12}$ a.p.f.u. (Table 1). In accord with the refined site-scattering values and mean bond lengths (Table 5), we assign Si to the fully occupied $\text{Si}(1-4)$ sites in the ordered part of the structure, Si_4 a.p.f.u. (Table 6). This leaves us with $\text{Si}_{0.65}$ and $\text{P}_{3.12}$ a.p.f.u. (with total scattering 55.9 e.p.f.u. from EMPA). The $T(1,2)$ sites occur in the disordered part of the structure, they have scattering of 27.0 and 23.4 e.p.f.u. (total refined scattering 50.4 e.p.f.u.), with $\langle T-\text{Anion} \rangle 1.54 \text{ \AA}$ (Table 5). Hence we assign $\text{P}_{1.56}\text{Si}_{0.33}\square_{1.11}$ ($\square$ = vacancy) to each of the $T(1,2)$ sites, which gives $T(1,2)$ total = $\text{P}_{3.12}\text{Si}_{0.66}\square_{2.22}$ a.p.f.u. and a total scattering of 56.04 e.p.f.u.

B sites

Ten B sites are coordinated by three O atoms. The chemical analysis gives $\text{B}_{8.89}$ a.p.f.u.. (Table 1). We assign B_8 a.p.f.u.. to the four $\text{B}(1-4)$ sites in the ordered part of the structure, with $\langle \text{B}(1-4)-\text{O} \rangle = 1.37 \text{ \AA}$ (Table 5). There are six $\text{B}(5-10)$ sites in the disordered part of the structure, and they are each characterized by a scattering of ≤ 1 el. We consider the $\text{B}(5-10)$ sites 16.7% occupied by B and assign $\text{B}_{0.167}\square_{0.833}$ a.p.f.u. to each of these sites (Table 6). The assigned B contents for the $\text{B}(1-4)$ and $\text{B}(5-10)$ sites are B_8 and $(\text{B}_{1.67}\square_5)$ with a total $(\text{B}_9\square_5)$ a.p.f.u.

A sites

In the ordered part of the structure, the $[12]$ -coordinated $A(1)$ site has a refined scattering of 168 e.p.f.u. and we assign Ba_3 a.p.f.u. to the $A(1)$ site (Tables 5,6). In the disordered part of the structure, the $A(2)$ site splits into three sites, $A(2A)$, $A(2B)$, $A(2C)$, with a scattering of ~ 36.96 e.p.f.u. each. These sites occur at short distances from each other and can be only partly occupied. We were unable to locate all coordinating anions for the $A(2A-C)$ sites, and the coordination numbers of the $A(2A)$, $A(2B)$ and $A(2C)$ sites are [6], [7] and [8] respectively, lower than [12] for the $A(1)$ site (Table 5). We assign $(\text{Ba}_{0.66}\square_{2.34})$ a.p.f.u. to each of the three $A(2A-C)$ sites.

TABLE 4. Anisotropic displacement parameters for selected atoms in byzantievite.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
<i>D</i> (1)	0.024(3)	0.019(3)	0.032(3)	0.005(2)	0.002(2)	0.007(2)	0.0261(14)
<i>D</i> (2)	0.013(3)	0.013(3)	0.018(5)	0	0	0.0067(13)	0.0149(19)
<i>D</i> (3)	0.015(2)	0.015(2)	0.000(4)	0	0	0.0077(12)	0.0103(18)
<i>D</i> (4)	0.017(3)	0.017(3)	0.003(4)	0	0	0.0086(13)	0.0123(18)
<i>D</i> (5)	0.010(2)	0.010(2)	0.017(5)	0	0	0.0048(12)	0.0120(18)
<i>D</i> (6)	0.012(2)	0.016(2)	0.017(3)	−0.0021(19)	0.0024(19)	0.0047(18)	0.0160(12)
<i>D</i> (7)	0.022(5)	0.049(6)	0.050(8)	0.008(5)	0.014(4)	0.017(4)	0.040(4)
<i>D</i> (8)	0.033(5)	0.029(5)	0.079(9)	−0.003(5)	−0.005(5)	0.009(4)	0.050(4)
<i>D</i> (9)	0.000(11)	0.000(11)	0.000(13)	−0.026(10)	−0.033(10)	−0.020(10)	0.009(6)
<i>D</i> (10)	0.020(10)	0.023(12)	0.000(14)	−0.001(9)	−0.007(11)	0.034(9)	0.004(5)
<i>D</i> (11)	0.019(10)	0.011(10)	0.000(12)	−0.024(9)	−0.038(9)	0.025(8)	0.003(5)
<i>D</i> (12)	0.018(15)	0.000(13)	0.011(16)	0.005(12)	0.007(13)	−0.037(14)	0.028(10)
<i>D</i> (13)	0.000(14)	0.000(14)	0.08(3)	−0.011(16)	0.014(15)	−0.015(10)	0.032(11)
<i>D</i> (14)	0.000(12)	0.15(4)	0.016(19)	−0.05(2)	−0.014(13)	0.037(17)	0.057(14)
<i>M</i> (1)	0.0201(17)	0.0201(17)	0.029(3)	0	0	0.0101(9)	0.0232(14)
<i>M</i> (2)	0.038(2)	0.047(2)	0.0114(19)	−0.0026(18)	−0.0029(18)	0.0252(18)	0.0304(10)
<i>M</i> (3)	0.0007(16)	0.0007(16)	0.034(4)	0	0	0.0003(8)	0.0119(14)
<i>M</i> (4)	0.0168(16)	0.0168(16)	0.011(3)	0	0	0.0084(8)	0.0149(12)
<i>M</i> (5)	0.0261(18)	0.0160(17)	0.035(2)	−0.0007(16)	−0.0004(17)	0.0106(15)	0.0257(10)
<i>M</i> (6)	0.0120(16)	0.0126(16)	0.019(2)	−0.0034(14)	−0.0018(15)	0.0081(13)	0.0138(9)
<i>M</i> (7)	0.036(2)	0.046(2)	0.011(2)	0.0030(18)	0.0034(18)	0.014(2)	0.0339(11)
<i>M</i> (8)	0.0175(18)	0.0175(18)	0.012(3)	0	0	0.0088(9)	0.0156(13)
<i>M</i> (9)	0.0373(18)	0.0377(19)	0.026(2)	0.0022(15)	0.0018(16)	0.0216(16)	0.0324(10)
<i>M</i> (10)	0.0373(18)	0.0377(19)	0.026(2)	0.0022(15)	0.0018(16)	0.0216(16)	0.0324(10)
<i>M</i> (11A)	0.0373(18)	0.0377(19)	0.026(2)	0.0022(15)	0.0018(16)	0.0216(16)	0.0324(10)
<i>M</i> (11B)	0.0373(18)	0.0377(19)	0.026(2)	0.0022(15)	0.0018(16)	0.0216(16)	0.0324(10)
<i>M</i> (11C)	0.0373(18)	0.0377(19)	0.026(2)	0.0022(15)	0.0018(16)	0.0216(16)	0.0324(10)
<i>M</i> (12A)	0.0373(18)	0.0377(19)	0.026(2)	0.0022(15)	0.0018(16)	0.0216(16)	0.0324(10)
<i>M</i> (12B)	0.0373(18)	0.0377(19)	0.026(2)	0.0022(15)	0.0018(16)	0.0216(16)	0.0324(10)
<i>M</i> (12C)	0.0373(18)	0.0377(19)	0.026(2)	0.0022(15)	0.0018(16)	0.0216(16)	0.0324(10)
Si(1)	0.034(4)	0.034(4)	0.057(8)	0	0	0.0171(18)	0.042(3)
Si(2)	0.034(4)	0.034(4)	0.057(8)	0	0	0.0171(18)	0.042(3)
Si(3)	0.034(4)	0.034(4)	0.057(8)	0	0	0.0171(18)	0.042(3)
Si(4)	0.034(4)	0.034(4)	0.057(8)	0	0	0.0171(18)	0.042(3)
<i>T</i> (1)	0.009(7)	0.025(8)	0.023(11)	−0.003(7)	0.007(7)	0.001(6)	0.022(4)
<i>T</i> (2)	0.000(7)	0.010(8)	0.004(9)	−0.011(6)	0.010(6)	−0.006(6)	0.009(4)
<i>A</i> (1)	0.0186(10)	0.0205(10)	0.0254(12)	0.0008(9)	−0.0004(10)	0.0102(9)	0.0213(6)
<i>A</i> (2A)	0.028(3)	0.029(3)	0.010(3)	0.002(3)	−0.011(3)	0.019(2)	0.0202(15)
<i>A</i> (2B)	0.028(3)	0.029(3)	0.010(3)	0.002(3)	−0.011(3)	0.019(2)	0.0202(15)
<i>A</i> (2C)	0.028(3)	0.029(3)	0.010(3)	0.002(3)	−0.011(3)	0.019(2)	0.0202(15)

Therefore the *A*(2A–C) sites are occupied by (Ba_{1.98}□_{7.02}) a.p.f.u. The total refined scattering and calculated scattering at the *A* sites is 278.88 e.p.f.u., the total cation content is (Ba_{4.98}□_{7.02}) a.p.f.u., in good agreement with Ba_{5.05} a.p.f.u. from the chemical analysis (Table 1).

D sites

Each of the 14 *D* sites is surrounded by an octahedral array of anions and *D*–anion bond

lengths vary from 1.88 to 2.22 Å (Table 5). Total refined scattering for the *D*(1–14) sites is 470.42 e.p.f.u. and 488.12 e.p.f.u. for (Ti_{12.31}Nb_{5.30})Σ_{17.61} from chemical analysis (Table 1). From the empirical formula, Ti:Nb = 2.33:1, and we assigned Ti and Nb using this particular ratio to the fully occupied *D*(1–6) sites in the ordered part of the structure: (Ti_{2.10}Nb_{0.90}) a.p.f.u. to each of the *D*(1,6) sites and (Ti_{0.70}Nb_{0.30}) a.p.f.u. to each of the *D*(2–4) sites (Table 6). For the

TABLE 5. Selected atomic distances* (Å) in byzantievite.

$D(1)-O(16)_1$	1.871(9)	$D(2)-O(14)$	$1.870(1) \times 3$	$D(4)-O(17)$	$1.910(1) \times 3$	$D(6)-O(16)$	1.900(1)
$D(1)-O(9)$	1.97(2)	$D(2)-O(6)_5$	$2.12(3) \times 3$	$D(4)-O(7)_7$	$2.10(2) \times 3$	$D(6)-O(12)_2$	1.92(2)
$D(1)-O(18)_2$	1.99(2)	$<D(2)-O>$	2.00	$<D(4)-O>$	2.01	$D(6)-O(17)_3$	1.985(9)
$D(1)-O(18)$	2.02(2)					$D(6)-O(12)$	2.00(3)
$D(1)-O(14)_3$	2.06(1)	$D(3)-O(15)_6$	$1.82(2) \times 3$	$D(5)-O(13)_{18}$	$1.870(1) \times 3$	$D(6)-O(10)_2$	2.05(2)
$D(1)-O(13)_4$	2.07(1)	$D(3)-O(11)_6$	$2.21(2) \times 3$	$D(5)-O(5)_9$	$2.17(2) \times 3$	$D(6)-O(15)_{10}$	2.08(2)
$<D(1)-O>$	2.00	$<D(3)-O>$	2.02	$<D(5)-O>$	2.02	$<D(6)-O>$	1.99
$D(7)-^bO(32)_{11}$	1.89(1)	$D(8)-^bO(38)_{12}$	1.98(2)	$D(9)-^cO(57)$	1.800(1)	$D(10)-^aO(44)_3$	1.95(1)
$D(7)-^bO(34)_{11}$	1.94(2)	$D(8)-^bO(43)_{13}$	2.00(1)	$D(9)-^cO(50)$	1.800(1)	$D(10)-^aO(44)_2$	2.00(1)
$D(7)-^bO(33)_{11}$	1.96(1)	$D(8)-^bO(36)_{13}$	2.00(1)	$D(9)-^cO(59)$	1.81(1)	$D(10)-^cO(48)$	2.07(4)
$D(7)-^bO(35)_{11}$	1.99(2)	$D(8)-^bO(40)_{12}$	2.00(1)	$D(9)-^bO(64)_{14}$	1.90(1)	$D(10)-^cO(52)$	2.07(4)
$D(7)-^bO(41)_{11}$	1.99(1)	$D(8)-^bO(37)_{13}$	2.00(1)	$D(9)-^cO(64)_{15}$	2.15(1)	$D(10)-^cO(58)$	2.10(5)
$D(7)-^bO(39)_{11}$	2.00(1)	$D(8)-^bO(42)_{13}$	2.21(1)	$D(9)-^cO(53)$	2.20(1)	$D(10)-^cO(59)$	2.22(3)
$<D(7)-O>$	1.96	$<D(8)-O>$	2.03	$<D(9)-O>$	1.95	$<D(10)-O>$	2.07
$D(11)-^cO(58)$	1.80(1)	$D(12)-^cO(50)$	1.855(8)	$D(13)-^cO(62)$	1.80(1)	$D(14)-^cO(60)$	1.85(1)
$D(11)-^cO(47)$	1.807(7)	$D(12)-^aO(46)_{14}$	1.900(1)	$D(13)-^cO(48)$	1.80(1)	$D(14)-^cO(61)$	1.90(1)
$D(11)-^cO(63)_{16}$	1.98(3)	$D(12)-^cO(62)$	1.970(1)	$D(13)-^aO(49)_2$	1.80(1)	$D(14)-^cO(47)$	1.954(8)
$D(11)-^cO(51)$	2.15(1)	$D(12)-^cO(60)$	1.99(8)	$D(13)-^cO(61)$	1.85(1)	$D(14)-^cO(54)$	2.000(1)
$D(11)-^cO(63)_{17}$	2.20(1)	$D(12)-^cO(56)$	2.000(1)	$D(13)-^aO(49)_3$	2.12(7)	$D(14)-^aO(45)_{16}$	2.01(1)
$D(11)-^cO(57)$	2.20(2)	$D(12)-^aO(46)_{15}$	2.100(1)	$D(13)-^cO(55)$	2.150(1)	$D(14)-^aO(45)_{17}$	2.01(1)
$<D(11)-O>$	2.02	$<D(12)-O>$	1.97	$<D(13)-O>$	1.92	$<D(14)-O>$	1.95
$M(1)-O(1)$	2.210(5)	$M(2)-O(23)_{16}$	2.35(1)	$M(3)-^aO(28)_7$	2.34(3)	$M(5)-F(1)_{22}$	2.293(8)
$M(1)-O(22)_3$	2.47(2)	$M(2)-O(8)_3 \times 3$	2.47(2)	$M(3)-O(11)_6 \times 3$	2.53(2)	$M(5)-O(20)_{16}$	2.35(1)
$M(1)-O(17)_7$	2.58(2)	$M(2)-O(22)_2 \times 3$	2.49(2)	$M(3)-O(26)_6 \times 3$	2.57(2)	$M(5)-O(11)$	2.42(3)
$M(1)-O(23)_5$	2.849(9)	$M(2)-O(29)_{21} \times 3$	2.50(2)	$M(3)-O(23)_6 \times 3$	2.83(1)	$M(5)-O(12)_2$	2.47(3)
$<M(1)-O>$	2.59	$M(2)-O(20)_2$	2.58(2)	$<M(3)-O>$	2.61 [10]	$M(5)-O(7)$	2.47(2)
		$M(2)-O(26)_{16}$	2.58(2)			$M(5)-O(22)_2$	2.48(2)
		$M(2)-O(20)$	2.60(3)	$M(4)-O(3)$	2.195(6)	$M(5)-O(10)_2$	2.56(2)
		$M(2)-O(2)_3$	2.74(2)	$M(4)-O(25)$	2.38(2)	$M(5)-O(10)_3$	2.59(2)
$M(2)-^aO(28)_{11}$		$M(2)-^aO(28)_{11}$	2.93(7)	$M(4)-O(6)_{17} \times 3$	2.55(2)	$<M(5)-O>$	2.45
$<M(2)-O>$		$<M(2)-O>$	¹⁸ 2.54 ¹⁹ 2.58	$M(4)-O(24)_7$	2.73(2)		
				$<M(4)-O>$	2.52		

$M(6)-O(18)$	2.230(1)	$M(7)-O(31)_6$	2.48(1)	$M(8)-^aO(27)_{26}$	2.21(1)	$M(9)-^bO(42)_3$	2.32(3)
$M(6)-F(2)_{23}$	2.287(8)	$M(7)-O(19)$	2.49(3)	$M(8)-O(5)_9$	2.51(2)	$M(9)-^bO(36)_3$	2.35(3)
$M(6)-O(21)_{24}$	2.31(2)	$M(7)-O(24)_2$	2.51(2)	$M(8)-O(21)_9$	2.52(2)	$M(9)-O(2)_3$	2.37(2)
$M(6)-O(6)_{24}$	2.44(2)	$M(7)-O(30)_{25}$	2.51(2)	$M(8)-O(24)_9$	2.77(2)	$M(9)-O(20)$	2.43(2)
$M(6)-O(5)_{24}$	2.44(2)	$M(7)-O(25)$	2.63(3)	$<M(8)-\phi>$	2.56	$M(9)-O(29)_{27}$	2.62(2)
$M(6)-O(25)_{22}$	2.48(2)	$M(7)-O(4)$	2.69(2)			$M(9)-^bO(37)_3$	2.64(3)
$M(6)-O(9)_3$	2.56(2)	$M(7)-O(19)_3$	2.69(2)			$M(9)-O(8)_2$	2.63(2)
$M(6)-O(9)$	2.65(2)	$M(7)-O(21)_{18}$	2.69(2)			$M(9)-O(29)_8$	2.66(2)
$<M(6)-\phi>$	2.42	$M(7)-^bO(27)_{25}$	2.84(3)			$M(9)-O(2)_{15}$	2.79(2)
		$<M(7)-\phi>$	^[8] 2.59 ^[8] 2.61			$<M(9)-\phi>$	3.00(2)
							^[10] 2.64 ^[10] 2.58
$M(10)-O(19)_3$	2.43(2)						
$M(10)-^bO(39)_{11}$	2.49(1)						
$M(10)-O(30)_{28}$	2.61(1)	$M(11A)-^cO(53)_{29}$	2.28(3)	$M(11B)-^cO(52)_{11}$	2.25(1)	$M(11C)-^cO(53)_{12}$	2.25(3)
$M(10)-O(31)_6$	2.63(1)	$M(11A)-O(4)_{10}$	2.29(2)	$M(11B)-^cO(51)_{11}$	2.31(2)	$M(11C)-^cO(51)_{12}$	2.36(2)
$M(10)-O(4)$	2.66(2)	$M(11A)-^cO(52)_{29}$	2.32(1)	$M(11B)-O(4)$	2.32(2)	$M(11C)-O(30)_{31}$	2.45(2)
$M(10)-O(31)_{30}$	2.67(2)	$M(11A)-O(30)_{31}$	2.39(2)	$M(11B)-O(31)_6$	2.50(2)	$M(11C)-O(31)_{42}$	2.50(3)
$M(10)-O(4)_{15}$	2.74(2)	$M(11A)-^cO(59)_{29}$	2.63(1)	$M(11B)-^cO(58)_{11}$	2.60(15)	$M(11C)-^cO(57)_{12}$	2.53(5)
$M(10)-O(30)_{30}$	2.78(1)	$M(11A)-^cO(53)_{12}$	2.76(3)	$M(11B)-^cO(52)_{28}$	2.65(1)	$M(11C)-^cO(53)_{29}$	2.60(4)
$M(10)-^bO(41)_{11}$	2.85(1)	$M(11A)-^cO(52)_{32}$	2.79(1)	$M(11B)-^cO(51)_{33}$	2.77(2)	$M(11C)-^cO(51)_{32}$	2.80(2)
$M(10)-^bO(35)_{52}$	2.87(1)	$<M(11A)-\phi>$	2.49	$<M(11B)-\phi>$	2.49	$<M(11C)-\phi>$	2.50
$<M(10)-\phi>$	^[10] 2.64 ^[10] 2.67						
$M(12A)-^cO(54)_{17}$	2.22(2)	$M(12B)-O(8)$	2.30(3)	$M(12C)-^cO(55)$	2.16(1)		
$M(12A)-^cO(60)_{17}$	2.29(10)	$M(12B)-^cO(54)_2$	2.33(2)	$M(12C)-^cO(56)$	2.20(1)		
$M(12A)-^cO(56)_{17}$	2.36(2)	$M(12B)-^cO(55)_2$	2.33(2)	$M(12C)-O(2)$	2.24(2)		
$M(12A)-O(2)_3$	2.42(3)	$M(12B)-O(29)_{43}$	2.44(3)	$M(12C)-O(8)$	2.37(2)		
$M(12A)-O(29)_{21}$	2.48(3)	$M(12B)-^cO(55)$	2.61(2)	$M(12C)-^cO(62)$	2.45(3)		
$M(12A)-^cO(56)_3$	2.63(2)	$M(12B)-^cO(54)_{74}$	2.76(2)	$M(12C)-^cO(56)_{14}$	2.79(1)		
$M(12A)-^cO(54)$	2.87(2)	$M(12B)-^cO(61)_2$	2.78(13)	$M(12C)-^cO(55)_2$	2.81(1)		
$<M(12A)-\phi>$	2.47	$<M(12B)-\phi>$	2.51	$<M(12C)-\phi>$	2.43		
$Si(1)-O(1)$	1.572(1)	$Si(3)-O(30)_3$	1.590(1)	$\pi(1)-O(22)_2$	1.54(1)	$\pi(2)-O(24)_{18}$	1.54(1)
$Si(1)-O(2)$	1.62(1)	$Si(3)-^aO(27)_3$	1.62(1)	$\pi(1)-O(26)_{24}$	1.540(1)	$\pi(2)-O(25)_2$	1.54(1)
$<Si(1)-O>$	1.61	$<Si(3)-O>$	1.60	$\pi(1)-O(23)_{10}$	1.540(1)	$\pi(2)-O(21)_{18}$	1.54(1)
				$\pi(1)-O(20)$	1.54(1)	$\pi(2)-O(19)$	1.55(1)
				$<\pi(1)-O>$	1.54	$<\pi(2)-O>$	1.54
$Si(2)-O(4)$	1.597(9)	$Si(4)-O(29)_{17}$	1.60(1)				
$Si(2)-O(3)$	1.600(1)	$Si(4)-^aO(28)_{16}$	1.60(1)				
$<Si(2)-O>$	1.598	$<Si(4)-O>$	1.60				

B(1)–O(7)	1.37(1)	B(2)–O(9) ²⁰	1.37(1)	B(3)–O(8) ₁₁	1.378(9)	× 3	B(7)– ^b O(38) ₁₁	1.370(1)	× 3
B(1)–O(10) ¹⁹	1.37(1)	B(2)–O(6)	1.37(1)	B(4)–O(31) ₇	1.370(1)	× 3	B(8)– ^b O(34) ₆	1.370(1)	× 3
B(1)–O(11)	1.37(1)	B(2)–O(5)	1.37(1)	B(5)– ^b O(43) ₆	1.370(1)	× 3	B(9)– ^b O(32)	1.370(1)	× 3
<B(1)–O>	1.37	<B(2)–O>	1.37	B(6)– ^b O(40) ₃	1.370(1)	× 3	B(10)– ^b O(33) ₁₁	1.370(1)	× 3
A(1)–O(17) ₁₅	2.79(2)	A(2A)– ^b O(34) ₃₃	2.37(3)	A(2B)– ^b O(38) ₂₉	2.60(3)		A(2C)– ^b O(40) ₃₁	2.62(1)	
A(1)–O(15)	2.82(3)	A(2A)– ^b O(43) ₁₁	2.37(3)	A(2B)– ^b O(33) ₂₉	2.66(2)		A(2C)– ^b O(40) ₃₉	2.66(2)	
A(1)–O(13) ₃₄	2.849(9)	A(2A)– ^b O(34) ₁₁	2.90(3)	A(2B)– ^b O(33) ₃₂	2.67(3)		A(2C)– ^b O(32) ₂₉	2.90(2)	
A(1)–O(14) ₃₅	2.86(1)	A(2A)– ^b O(38) ₂₈	3.10(2)	A(2B)– ^b O(38) ₃₁	2.75(2)		A(2C)– ^b O(34) ₁₂	2.93(3)	
A(1)–O(13) ₃₆	2.877(9)	A(2A)– ^b O(33) ₁₁	3.17(3)	A(2B)– ^b O(43) ₃₂	2.94(3)		A(2C)– ^b O(32) ₁₂	3.02(2)	
A(1)–O(14) ₃₇	2.88(2)	A(2A)– ^b O(40) ₄₀	3.19(2)	A(2B)– ^b O(40) ₃₁	3.07(1)		A(2C)– ^b O(33) ₂₉	3.15(2)	
A(1)–O(15) ₁₇	2.93(2)	<A(2A)–φ>	2.85	A(2B)– ^b O(34) ₁₂	3.24(3)		A(2C)– ^b O(43) ₃₂	3.20(2)	
A(1)–O(17)	2.94(1)			<A(2B)–φ>	2.85		A(2C)– ^b O(38) ₃₁	3.27(2)	
A(1)–O(12) ₂₀	2.99(3)						<A(2C)–φ>	2.97	
A(1)–O(18) ₃₈	3.11(1)								
A(1)–O(16) ₁₆	3.18(3)								
A(1)–O(16) ₂₀	3.23(3)								
<A(1)–O>	2.95								
D(7)–D(9) ₁₁	2.30(1)	D(8)–D(12) ₁₃	2.280(8)	D(9)–D(9) _{15,14}	1.546(6)		D(12)–D(12) _{15,14}	1.554(2)	
D(7)–D(10) ₁₁	2.26(1)	D(8)–D(13) ₁₃	2.16(2)	D(9)–B(9)	0.942(4)		D(12)–B(6)	0.898(1)	
D(7)–D(11) ₁₁	2.26(1)	D(8)–D(14) ₁₃	2.03(1)	D(10)–D(10) _{2,3}	1.54(2)		D(13)–D(13) _{2,3}	1.74(3)	
D(7)–M(11A) ₁₇	3.14(2)	D(8)–M(12A) ₃₃	3.03(2)	D(10)–B(10) ₂₂	1.01(1)		D(13)–B(7) ₂₂	1.00(2)	
D(7)–M(11B) ₁₆	2.99(2)	D(8)–M(12B) ₁₂	3.04(2)	D(11)–D(11) _{16,17}	1.53(2)		D(14)–D(14) _{16,17}	2.04(2)	
D(7)–M(11C) ₁₆	3.06(2)	D(8)–M(12C) ₁₃	2.98(2)	D(11)–B(8) ₄₄	0.88(2)		D(14)–B(5) ₄₄	1.18(1)	
M(9)–M(12A) ₂₄	2.76(2)	M(10)–M(11A) ₁₇	2.69(1)	M(11A)–M(11B) ₁₉	1.39(2)		M(12A)–M(12B) ₃	1.36(2)	
M(9)–M(12B) ₂	2.63(2)	M(10)–M(11B)	2.68(2)	M(11A)–M(11C)	1.35(2)		M(12A)–M(12C) ₃	1.34(2)	
M(9)–M(12C) ₃	2.66(2)	M(10)–M(11C) ₁₆	2.62(2)	M(11B)–M(11C) ₁₈	1.52(3)		M(12B)–M(12C)	1.41(2)	
A(2A)–A(2B) ₁₈	1.11(1)	A(2B)–A(2C)	0.95(2)						
A(2A)–A(2C) ₁₈	1.12(2)								

φ = O, OH, F, H₂O,^{a, b, c} = anion site is occupied at 33, 67, 17% respectively [e.g. ^bO(42) = 67% occupied]. For the M(2, 7) and M(9, 10) polyhedra, two mean bond-lengths are given (depending on a coordination number shown in superscript brackets); e.g. M(2): ⁽⁸⁾2.54 and ⁽⁹⁾2.58 Å correspond to 8 fully-occupied anion sites and 8 fully-occupied anion sites plus O(28) occupied by O atoms at 33%. * Impossible to detect all ligands for A(2A–C), M(11A–C), M(12A–C) cations. Symmetry operators: **1**: x, y, z + 1; **2**: –y + 1, x – y, z; **3**: –x + y + 1, –x + 1, z; **4**: –x + y + 1/3, –x + 4/3, z + 1/3; **5**: –x + y – 1, –x, z; **6**: x – 1/3, y – 2/3, z + 1/3; **7**: x – 1, y – 1, z; **8**: –x + y + 1/3, –x + 2/3, z – 1/3; **9**: –y + 2/3, x – y + 1/3, z – 2/3; **10**: x + 1, y, z; **11**: –x + y + 1/3, –x + 2/3, z + 2/3; **12**: x + 1/3, y – 1/3, z – 1/3; **13**: –y + 4/3, x – y + 2/3, z + 2/3; **14**: –x + y, –x, z; **15**: –y, x – y, z; **16**: –x + y, –x + 1, z; **17**: –y + 1, x – y + 1, z; **18**: x, y – 1, z; **19**: x, y + 1, z; **20**: x – 1, y, z; **21**: x + 1/3, y – 1/3, z – 1/3; **22**: x + 2/3, y + 1/3, z – 2/3; **23**: x + 2/3, y + 1/3, z + 1/3; **24**: –x + 2/3, x – y + 1, z; **25**: x – 2/3, y – 1/3, z + 2/3; **26**: –y, x – y – 1, z; **27**: –y + 7/3, x – y + 5/3, z – 1/3; **28**: –y + 1/3, x – y – 1/3, z + 2/3; **29**: –y + 1/3, x – y + 2/3, z + 2/3; **30**: –x + y + 2/3, –x + 4/3, z + 1/3; **31**: x – 2/3, y + 2/3, z + 2/3; **32**: –x + y + 1/3, –x + 5/3, z + 2/3; **33**: x – 1/3, y – 1/3, z – 2/3; **34**: x – 1/3, y + 1/3, z – 2/3; **35**: x, y, z – 1; **36**: –x + y + 2/3, –x + 4/3, z – 2/3; **37**: –y, x – y, z – 1; **38**: x – 1, y, z – 1; **39**: –x + y + 4/3, –x + 5/3, z + 2/3; **40**: –x + y + 4/3, –x + 2/3, z + 2/3; **41**: x – 2/3, y – 1/3, z – 1/3; **42**: x – 1/3, y + 1/3, z + 1/3; **43**: –y + 4/3, x – y

D(1–6) sites, the total cation content is (Ti_7Nb_3) a.p.f.u. In the disordered part of the structure, the low scattering (13.9 e.p.f.u.) at each of the six *D*(9–14) sites indicates that these (Ti,Nb) sites are 17% occupied (Table 6). Hence we assigned $(\text{Ti}_{0.35}\text{Nb}_{0.15}\square_{2.50})$ a.p.f.u. to all six *D*(9–14) sites, giving in total $(\text{Ti}_{2.10}\text{Nb}_{0.90}\square_{15})$ a.p.f.u. During structure refinement, the site occupancies for the *D*(1–6) and *D*(9–14) sites were fixed at the values assigned above and site occupancies for the *D*(7,8) sites were unconstrained; they refined to 51(2) and 59(2) e.p.f.u. respectively, with a total of 110 e.p.f.u. The *D*(1–6) and *D*(9–14) sites accommodate $\text{Ti}_{9.10}\text{Nb}_{3.90}$ a.p.f.u., the empirical formula has $\text{Ti}_{12.31}\text{Nb}_{5.30}$ a.p.f.u., and we are left with $\text{Ti}_{3.21}\text{Nb}_{1.40}$ a.p.f.u. (128 e.p.f.u.) for the two *D*(7,8) sites. The difference between total scattering from chemical analysis and structure refinement is $128 - 110 = 18$ e.p.f.u., ~16% of the lesser value (from structure refinement). We suggest that this high value is due to accumulated errors during structure refinement of the disordered cation sites. In an attempt to accommodate this discrepancy for the *D*(7,8) sites, we assign to them cations with a scattering intermediate between that from chemical analysis and that from structure refinement, $(128 + 110)/2 = 119$ e.p.f.u. We assign $(\text{Ti}_{1.38}\text{Nb}_{0.70}\square_{0.92})$ a.p.f.u. to each of the *D*(7,8) sites (69% occupancy) which gives total site population and total scattering for these two sites of $(\text{Ti}_{2.76}\text{Nb}_{1.40}\square_{1.84})$ a.p.f.u. and 118 e.p.f.u. (Table 6). The values for total refined and total calculated scattering at the *D* sites are 470.42 and 478.10 e.p.f.u., respectively. The total assigned cation content at the *D* sites is $(\text{Ti}_{11.86}\text{Nb}_{5.30}\square_{16.84})$ a.p.f.u. (Table 6). The difference between (Ti,Nb) content from site assignment, $(\text{Ti}_{11.86}\text{Nb}_{5.30})_{\Sigma 17.16}$, and chemical analysis, $(\text{Ti}_{12.31}\text{Nb}_{5.30})_{\Sigma 17.61}$, is 0.45 a.p.f.u.

M sites

There are 12 *M* sites in the crystal structure. Their coordination numbers vary from [7] to [10], their mean bond lengths vary from 2.42 to 2.67 Å, and they have a total refined scattering of 867.24 e.p.f.u. (Table 6). The chemical analysis gives $[(\text{Ca}_{8.99}\text{Sr}_{0.96}\text{Fe}_{0.42}\text{Na}_{0.20})_{\Sigma 10.57}(\text{Ce}_{3.46}\text{La}_{1.54}\text{Nd}_{1.20}\text{Pr}_{0.30}\text{Sm}_{0.26}\text{Dy}_{0.41}\text{Gd}_{0.32}\text{Th}_{0.39}\text{U}_{0.17})_{\Sigma 8.05}\text{Y}_{3.53}]_{\Sigma 22.15}$ (Table 1), equivalent to 859.63 e.p.f.u. The difference between the site-scattering from structure refinement and chemical analysis for the group of cations listed above is 7.61 e.p.f.u., i.e.

0.9% compared to the total scattering calculated from the chemical analysis. Further on, we will use *REE* notation to describe a set of trivalent rare-earth elements, $(\text{Ce}_{3.46}\text{La}_{1.54}\text{Nd}_{1.20}\text{Pr}_{0.30}\text{Sm}_{0.26}\text{Dy}_{0.41}\text{Gd}_{0.32})_{\Sigma 7.49}$ a.p.f.u., which is characterized by an average scattering power of 58.99 el. We will use 58.99 el to calculate the site-scattering from *REE* at the *M*(1–12) sites (see footnote, Table 6). First, based on observed mean bond lengths (Table 5) and refined individual site-scattering values, we assigned specific cations to the fully-occupied *M*(1–8) sites in the ordered part of the structure. The total cation content assigned to the *M*(1–8) sites is $\text{Ca}_{7.75}\text{REE}_{4.30}\text{Y}_{3.53}\text{Fe}_{0.42}$ a.p.f.u.; the refined and calculated site-scattering, 559.94 and 557.25 e.p.f.u. respectively, are in good agreement. We are left with $\text{Ca}_{1.24}\text{Sr}_{0.96}\text{Na}_{0.20}\text{REE}_{3.19}\text{Th}_{0.39}\text{U}_{0.17}$ (286.91 e.p.f.u. from chemical analysis) to assign to two *M*(9,10) plus six *M*(11A–C,12A–C) sites, with refined scattering $131.37 + 175.93 = 307.3$ e.p.f.u. The *M*(9,10) and *M*(11A–C,12A–C) sites are located in the disordered part of the structure, they occur at short distances from each other (Table 5) and must therefore be partly occupied. The *M*(9,10) sites share coordinating anions with the *D*(7,8) sites [69% occupied by (Ti,Nb)] and *T*(1,2) sites [63% occupied by P and Si]. We suggest that the occupancies of the *M*(9,10) sites are similar to those of the *D*(7,8) and *T*(1,2) sites, i.e. >50%. The six *M*(11A–C,12A–C) sites are disordered around threefold axes and must be occupied $\leq 33\%$. The *M*(11A–C,12A–C) sites share anions with the *D*(9–14) sites [17% occupied by (Ti,Nb)] and we propose that the *M*(11A–C,12A–C) sites are occupied also by cations at 17%. Thus (1) the two *M*(9,10) sites are occupied by $(\text{Ca}_{1.24}\text{REE}_{1.11}\text{Sr}_{0.96}\square_{2.69})$ a.p.f.u. (55% occupancy); (2) the six *M*(11A–C,12A–C) sites are occupied by $(\text{REE}_{2.08}\text{Th}_{0.39}\text{U}_{0.17}\text{Na}_{0.20}\square_{15.16})$ a.p.f.u. (17% occupancy) (Table 6).

We have assigned 22.15 a.p.f.u. to the 12 *M* sites, with a total calculated site-scattering of 859.65 e.p.f.u. (cf. 867.24 e.p.f.u. from structure refinement and 859.63 e.p.f.u. from chemical analysis).

Structure description

Cation sites

There are 50 cation sites in the crystal structure of byzantievite. Table 6 lists the cation sites, their constituent species, refined and calculated site-scattering values, a bond-valence sum and an

TABLE 6. Cation sites in the crystal structure of byzantievite.

Site	Multiplicity (a.p.f.u.)	Occupancy (%)	Assigned population (a.p.f.u.)	Refined site-scattering (e.p.f.u.)	Calculated site-scattering (e.p.f.u.)**	B.V. †† (v.u.)	A.C. ††
[12]A(1)	3	100	3 Ba	168	168	2.18	2
[6-8]A(2A-C)*†	3 × 3	22	(0.66 Ba + 2.34 □) × 3	36.96 × 3	36.96 × 3	<0.41>	0.44
ΣA			4.98 Ba + 7.02 □	278.88	278.88		
[4]Si(1)	1	100	1 Si	14	14	4.25	4
[4]Si(2)	1	100	1 Si	14	14	4.32	4
[4]Si(3)	1	100	1 Si	14	14	4.36	4
[4]Si(4)	1	100	1 Si	14	14	4.32	4
ΣSi			4 Si	42	42		
[4]T(1)	3	63	1.56 P + 0.33 Si + 1.11 □	27	28.02	3.32	3.17
[4]T(2)	3	63	1.56 P + 0.33 Si + 1.11 □	23.4	28.02	3.32	3.17
ΣT			3.12 P + 0.66 Si + 2.22 □	50.4	56.04		
[3]B(1)	3	100	3 B	15	15	2.97	3
[3]B(2)	3	100	3 B	15	15	2.97	3
[3]B(3)	1	100	1 B	5	5	2.97	3
[3]B(4)	1	100	1 B	5	5	2.97	3
[3]B(5-10)	1 × 6	16.7	(0.167 B + 0.833 □) × 6	0.835 × 6	0.835 × 6	<0.50>	0.5
ΣB			9 B + 5 □	45	45		
[6]D(1)	3	100	2.10 Ti + 0.90 Nb	83.15	83.1	4	4.3
[6]D(2-5)	1 × 4	100	(0.70 Ti + 0.30 Nb) × 4	27.68 × 4	27.70 × 4	<4.13>	4.3
[6]D(6)	3	100	2.10 Ti + 0.90 Nb	83.15	83.1	4.09	4.3
ΣD(1-6)			7 Ti + 3 Nb	277.02	277		
[6]D(7)	3	69	1.38 Ti + 0.70 Nb + 0.92 □	51(2)	59	2.88	3
[6]D(8)	3	69	1.38 Ti + 0.70 Nb + 0.92 □	59(2)	59	2.45	3
ΣD(7,8)			2.76 Ti + 1.40 Nb + 1.84 □	110	118		
[6]D(9-14)*	3 × 6	17	(0.35 Ti + 0.15 Nb + 2.50 □) × 6	13.90 × 6	13.85 × 6	<0.74>	0.72
ΣD(9-14)			2.10 Ti + 0.90 Nb + 15 □	83.4	83.1		
ΣD			11.86 Ti + 5.30 Nb + 16.84 □	470.42	478.1		

^[10] M(1)	1	100	0.50 Y + 0.25 REE** + 0.25 Ca	40.72	39.25	2.69	2.75
^[8,9] M(2)	3	100	1.86 Ca + 1.14 REE	104.4	104.45	2.4	2.38
^[10] M(3)	1	100	0.52 Ca + 0.25 Y + 0.23 REE	33.76	33.72	2.73	2.48
^[10] M(4)	1	100	1.0 Y	38.8	39	2.92	3
^[8] M(5)	3	100	1.41 Ca + 0.75 Y + 0.63 REE + 0.21 Fe ²⁺	104.4	100.07	2.38	2.46
^[8] M(6)	3	100	1.41 Ca + 0.78 Y + 0.60 REE + 0.21 Fe ²⁺	96.57	99.47	2.7	2.46
^[8,9] M(7)	3	100	1.86 Ca + 1.14 REE	104.4	104.45	2.1	2.38
^[10] M(8)	1	100	0.44 Ca + 0.31 REE + 0.25 Y	36.89	36.84	2.65	2.56
ΣM(1–8)			7.75 Ca + 4.30 REE + 3.53 Y + 0.42 Fe²⁺	559.94	557.25		
^[7–10] M(9)	3	55	0.72 REE + 0.62 Ca + 0.30 Sr + 1.36 □	69.77	66.27	1.62	1.33
^[7–10] M(10)	3	55	0.66 Sr + 0.62 Ca + 0.39 REE + 1.33 □	61.6	60.49	1.01	1.24
ΣM(9,10)			1.24 Ca + 1.11 REE + 0.96 Sr + 2.69 □	131.37	126.76		
^[7] M(11A)*†	3	17		34.45		0.39	0.48
^[7] M(11B)*†	3	17		31.32		0.41	0.48
^[7] M(11C)*†	3	17		22.45		0.29	0.48
^[7] M(12A)*†	3	17		26.28		0.43	0.48
^[7] M(12B)*†	3	17		27.67		0.35	0.48
^[7] M(12C)*†	3	17		33.76		0.58	0.48
ΣM(11,12)			2.08 REE + 0.39 Th + 0.17 U⁴⁺ + 0.20 Na + 15.16 □	175.93	175.65		
ΣM			8.99 Ca + 0.96 Sr + 0.42 Fe²⁺ + 0.20 Na + 7.49 REE + 0.39 Th + 0.17 U⁴⁺ + 3.53 Y + 17.85 □	867.24	859.65		
Cations total	(Ba_{4.98}□_{7.02})	{[(Ca_{8.99}Sr_{0.96}Fe_{0.42}²⁺Na_{0.20}Σ_{10.57} (REE**_{7.49}Th_{0.39}U_{0.17}⁴⁺)Σ_{8.05} Y_{3.53}]Σ_{22.15} □_{17.85}}				Total charge = 201.34⁺	
			[(Ti_{1.86}Nb_{5.30}Σ_{17.16} □_{16.84}Si₄(P_{3.12}S_{0.66} □_{2.22})(B₉ □₅)				

Coordination numbers are given in square brackets.

* sites A(2A–C), D(9–14), M(11A–C) and M(12A–C) occur at short distances with other cation sites and hence can be only partly occupied. ** in accord with chemical composition, REE = Ce_{3.46}La_{1.54}Nd_{1.20}Dy_{0.41}Gd_{0.32}Pr_{0.30}Sm_{0.26}, total 7.49 a.p.f.u., an average REE-scattering curve of 58.99 e[–] was used to calculate site-scattering; † not possible to detect all ligands of the cation; ‡ B.V.: bond valence (v.u. = valence unit) per 1 a.p.f.u. calculated using the parameters of Brown (1981); A.C.: aggregate charge per 1 a.p.f.u. M(11–12) sites, B.V. was calculated for the site-population Ce_{0.17}□_{0.83}, <AC> = 0.48 = [charge of ΣM(11,12)]/12.

aggregate charge at each site [except for the $M(11A-C, 12A-C)$ sites for which it was impossible to assign cation species]. Twenty three sites are fully occupied (100%): $Si(1-4)$ and $B(1-4)$ are occupied by Si and B respectively; the $A(1)$ site is occupied by Ba; $D(1-6)$ are occupied by Ti and Nb; $M(1-8)$ are occupied mainly by Ca, REE and Y with minor Fe^{2+} . Twenty seven sites are partly occupied: six sites are >50% occupied and 21 sites are <50% occupied. Consider first the sites with >50% occupancy: $T(1,2)$ are occupied at 63% by P and Si; $D(7,8)$ are occupied at 69% by Ti and Nb; $M(9)$ and $M(10)$ are occupied at 55% by Ca, REE and Sr. Consider secondly, the sites with <50% occupancy: $A(2A-C)$ are occupied by Ba at 22%; $B(5-10)$ are occupied by B at 16.7%; $D(9-14)$ are occupied by Ti and Nb at 17%; $M(11A-C)$ and $M(12A-C)$ are occupied by REE and minor Th, U^{4+} and Na at 17%. Table 6 shows good agreement between the calculated bond-valence sums incident at the cation sites and the aggregate charges at these sites, indicating (1) that assigned populations are correct, and (2) a total cation content of $(Ba_{4.98}\square_{7.02})\{[(Ca_{8.99}Sr_{0.96}Fe_{0.42}Na_{0.20})\Sigma_{10.57}(REE_{7.49}Th_{0.39}U_{0.17})\Sigma_{8.05}Y_{3.53}]\Sigma_{22.15}\square_{17.85}\}[(Ti_{11.86}Nb_{5.30})\Sigma_{17.16}\square_{16.84}]Si_4(P_{3.12}Si_{0.66}\square_{2.22})(B_9\square_5)$ and a total charge 201.34^+ (Table 6).

We can divide the 50 cation sites in the crystal structure of byzantievite (Table 6) into three main groups: (1) 23 sites with 100% occupancy: $Si(1-4)$, $B(1-4)$, $A(1)$, $D(1-6)$, $M(1-8)$; (2) six sites with >50% occupancy: $M(9,10)$, $T(1,2)$ and $D(7,8)$ where the site occupancy varies from 55 to 69%; (3) 21 sites with <50% occupancy: $B(5-10)$, $D(9-14)$; $M(11A-C)$, $M(12A-C)$, $A(2A-C)$, in which the site occupancy varies from 16.7 to 22%.

For simplicity and convenience of anion considerations, we will define an *occupancy* characterizing each of three groups of cation sites. The first group comprises fully occupied cation sites (100%) and the group 1 occupancy is 100%. The second group comprises the $M(9,10)$ (55%), $T(1,2)$ (63%) and $D(7,8)$ (69%) sites, and we calculate the group 2 occupancy based on sites occupied by small (P,Si) and medium (Ti,Nb) cations with a high charge (and strong bonds). The mean group 2 occupancy, $63 + 69 = 66\%$, can be approximated as 67% which allows rounding errors to be avoided where operating in hexagonal symmetry. The third group comprises the $B(5-10)$ (16.7%), $D(9-14)$ (17%), $M(11A-C)$

TABLE 7. Anion sites* in the crystal structure of byzantievite.

Site	Occupancy (%)	Assigned species (a.p.f.u.)	B.V.** (v.u.)	A.C.**	Site	Occupancy (%)	Assigned species (a.p.f.u.)	B.V.** (v.u.)	A.C.**
O(1)	100	1 O	1.82	2	O(32)	67	1.5 OH + 0.5 O + 1 □	0.82	0.83
O(2)	100	3 O	1.63	2	O(33)	67	1.5 OH + 0.5 O + 1 □	0.86	0.83
O(3)	100	1 O	1.75	2	O(34)	67	1.5 OH + 0.5 O + 1 □	0.96	0.83
O(4)	100	3 O	1.70	2	O(35)	67	2 OH + 1 □	0.44	0.67
O(5)	100	3 O	2.02	2	O(36)	67	2 OH + 1 □	0.68	0.67
O(6)	100	3 O	2.01	2	O(37)	67	2 OH + 1 □	0.58	0.67
O(7)	100	3 O	2.04	2	O(38)	67	1.5 OH + 0.5 O + 1 □	0.84	0.83
O(8)	100	3 O	1.75	2	O(39)	67	2 OH + 1 □	0.55	0.67
O(9)	100	3 O	2.13	2	O(40)	67	1.5 OH + 0.5 O + 1 □	0.86	0.83
O(10)	100	3 O	2.03	2	O(41)	67	2 OH + 1 □	0.44	0.67
O(11)	100	3 O	1.96	2	O(42)	67	2 OH + 1 □	0.57	0.67
O(12)	100	3 O	1.88	2	O(43)	67	1.5 OH + 0.5 O + 1 □	0.80	0.83
O(13)	100	3 O	1.90	2	ΣO(32–43)		3 O + 21 (OH) + 12 □		

Structure	Formula	Weight	Count	Formula	Weight	Count	Formula	Weight	Count	Formula	Weight	Count
O(14)	3 O	1.90	2									
O(15)	3 O	2.00	2									
O(16)	3 O	1.94	2									
O(17)	3 O	1.92	2									
O(18)	3 O	1.95	2									
ΣO(1–18)	50 O											
O(19)	2 O + OH	1.53	1.67									
O(20)	2 O + OH	1.51	1.67									
O(21)	2 O + OH	1.72	1.67									
O(22)	2 O + OH	1.73	1.67									
O(23)	2 O + OH	1.57	1.67									
O(24)	2 O + OH	1.41	1.67									
O(25)	2 O + OH	1.71	1.67									
O(26)	2 O + OH	1.69	1.67									
ΣO(19–26)	16 O + 8 (OH)											
O(27)	1 O	1.73	2									
O(28)	1 O	1.65	2									
O(29)	3 O	1.74	2									
O(30)	3 O	1.74	2									
O(31)	3 O	1.65	2									
ΣO(27–31)	11 O											
F(1)	1 F	1.14	1									
F(2)	1 F	1.17	1									
ΣF(1,2)	2 F											
Anions total: O ₈₀ [(OH) ₄₃ (H ₂ O) _{1.5} = 124.5 anions p.f.u.]												

* The O(1), O(3), F(1) and F(2) sites have a multiplicity of 1 a.p.f.u.; all other sites have a multiplicity of 3 a.p.f.u.; except for the F(1) and F(2) sites, it was impossible to distinguish between OH and F anion species; hence, OH = OH + F.

*** B.V.: Bond Valence (v.u. = valence unit) per 1 a.p.f.u. calculated using the parameters of Brown (1981).

A.C. = Aggregate Charge of an assigned species per 1 a.p.f.u.

(17%), $M(12A-C)$ (17%), $A(2A-C)$ (22%) sites, and we consider the group 3 occupancy to be 17%. In further discussion we consider three groups of cation sites, with 100%, 67% and 17% occupancy.

Anion sites

The 68 anion sites are listed in Table 7. There is considerable uncertainty in the individual occupancies of the anion sites in the crystal structure of byzantievite. However, what is certain is that the site occupancies of the anions are approximately equal to the occupancies of the cations to which they are bonded. We have divided the cation sites into three groups on the basis of their occupancy: 100%, 67% and 17%. We will consider analogous groups of anion sites and assign a constituent species to each anion site in accord with the group occupancy of the adjacent cation sites. Except for the $F(1)$ and $F(2)$ sites, we were unable to distinguish between OH and F at sites containing monovalent anions. Where below we assign OH, we consider both monovalent anions, OH and F to be implicit. Note that two groups of anions, $O(32-43)$ and $O(44-64)$, with 67% and (17 and 33%) occupancy, respectively, occur at short distances from each other and cannot, simultaneously, be occupied at a local scale.

Fully occupied anion sites

Consider first the $O(1-18)$ anion sites. These anions coordinate fully occupied cation sites (Table 5): $O(1-4)$ coordinate $Si(1-4)$ sites (plus one to three M sites); $O(5-11)$, $B(1-4)$ sites [plus a $D(1-6)$ site and two M sites]; $O(12-18)$, each anion coordinates four sites, two of the $D(1-6)$ sites and two of the $M(5)$, $M(6)$ and $A(1)$ sites. The bond-valence sums at $O(1-18)$ vary from 1.63 to 2.13 v.u. (valence unit) (Table 7), and we conclude that the $O(1-18)$ anion sites are fully occupied by O atoms. Consider secondly, the $O(19-26)$ anions. Each anion coordinates one of the $T(1,2)$ sites plus three M sites (Table 5) and receives its largest bond-valence contribution from a T cation. The $T(1,2)$ sites are each occupied by (P,Si) (67% occupancy, group 2) or vacancy (33%). Where a T site is occupied by P or Si (67%), the coordinating anions must be O atoms. Where the T site is vacant (33%), the coordinating anions are OH groups. Therefore, we assign $O_{0.67}OH_{0.33}$ [= (2O + OH) a.p.f.u.] to each of the $O(19-26)$ anion sites (Table 7). Note that the bond-valence sums

at the $O(19-26)$ anions (1.41–1.73 v.u.) are in close agreement with the aggregate charge per one a.p.f.u., $[2 \times 2 + 1]/3 = 1.67$. Finally, consider atoms $F(1)$ and $F(2)$: they are coordinated by three M cations and have incident bond-valence sums of ~ 1 v.u. each.

67% occupied anion sites

The $O(32,33,34,38,40,43)$ anions coordinate the $D(7,8)$ sites that are occupied by (Ti,Nb) (67% occupancy, group 2) and the $B(5-10)$ sites occupied by B (17% occupancy, group 2). The $O(32,33,34,38,40,43)$ anions occur at common vertices of $D(7,8)$ and $B(5-10)$ polyhedra. From the $D(7,8)$ and $B(5-10)$ atoms, they receive major bond-valence contributions. In accord with the 67% occupancy of the $D(7,8)$ sites, we assign 67% occupancy for the $O(32,33,34,38,40,43)$ sites: $\phi_{0.67}\square_{0.33}$, where ϕ = unspecified anion. There are three possible short-range order (SRO) arrangements involving $D(7,8)$, $B(5-10)$ and $O(32,33,34,38,40,43)$ atoms: (1) $D(7,8)$ and $B(5-10)$ sites are fully occupied by (Ti,Nb) and B (17% occupancy), and $\phi = O_{0.17}^{2-}$; (2) $D(7,8)$ sites are occupied by (Ti,Nb) and $B(5-10)$ sites are vacant, hence $\phi = OH_{0.50}$; (3) $D(7,8)$ and $B(5-10)$ sites are vacant, and $\phi = \square_{0.33}$. Therefore, we write the anion species at each of the $O(32,33,34,38,40,43)$ sites as $(OH)_{0.50}O_{0.17}\square_{0.33}$ which equals (1.5 OH + 0.5 O + 1 $\square$) a.p.f.u. (taking into account the multiplicity three for the formula unit) (Table 7).

Each of the $O(35,36,37,39,41,42)$ anion sites is adjacent to one of the $D(7,8)$ sites occupied by (Ti,Nb) at 67%. The $O(35,36,37,39,41,42)$ anions receive major bond-valence contributions from a $D(7,8)$ atom plus minor contributions from atoms at the $M(11,12)$ sites which are occupied mainly by REE at 17%. Using the SRO approach (see above), we consider these anion sites as occupied by OH groups at 67% and assign $(OH)_{0.67}\square_{0.33}$ to each of the $O(35,36,37,39,41,42)$ sites. The total anion content of the six $O(35,36,37,39,41,42)$ sites is therefore $(2\text{ OH} + 1\text{ } \square) \times 6$ a.p.f.u. (Table 7).

17% and 33% occupied anion sites

The $O(44-64)$ anions coordinate the $D(9-14)$ sites [$\sim 17\%$ occupied by (Ti,Nb)] and the $M(11A-C, 12A-C)$ sites (17% occupied by REE) (Tables 5, 6). As mentioned before, we were unable to locate all ligands of the $M(11A-C, 12A-C)$ cations. However, it is clear that the $O(44-64)$ anions receive major bond-valence contributions from the $D(9-14)$

cations and minor contributions from the $M(11A-C, 12A-C)$ cations.

Each of the 12 $O(47,48,51-62)$ anions coordinates one (Ti,Nb) atom at the $D(9-14)$ sites (17% occupancy) (Table 5), and therefore these anion sites are occupied at 17%. We assign $(OH)_{0.17}\square_{0.83}$ to each of the $O(47,48,51-62)$ sites. The total anion content of the 12 $O(47,48,51-62)$ sites is therefore $(0.5\ OH + 2.5\ \square) \times 12$ a.p.f.u. (Table 7).

The six anions, $O(44-46,49,63,64)$, are each bonded to one (Ti,Nb) atom at the $D(9-14)$ sites (with 17% occupancy). Each $D(9-14)$ cation is octahedrally coordinated and is bonded to two of the $O(44,45,46,49,63,64)$ anions (Table 5): $D(9) - O(64) \times 2$; $D(10) - O(44) \times 2$; $D(11) - O(63) \times 2$; etc. Therefore, occupancy of the six anion sites $O(44-46,49,63,64)$ must be twice that of the 17% occupancy of the $D(9-14)$ sites, ~33%. We assign $(OH)_{0.33}\square_{0.67}$ to each of the $O(44-46,49,63,64)$ sites. The total anion content of the six $O(44-46,49,63,64)$ sites is thus $(1\ OH + 2\ \square) \times 6$ a.p.f.u. (Table 7).

The $O(47,48,50)$ anions occur at $z \sim 0.167$, and they are adjacent to two of the $D(9-14)$ sites. Assuming that the (Ti,Nb) atoms are randomly distributed over the $D(9-14)$ sites, the probability of two [(Ti,Nb)(OH)₆] octahedra linking together is very low ($0.17^2 = 0.0289$). The coordinating anions will link only to one (Ti,Nb) atom and therefore they must be (H₂O) groups. Hence we assign $(H_2O)_{0.17}\square_{0.83}$ to each of the $O(47,48,50)$ sites. The total anion content of the three $O(47,48,50)$ sites is $(0.5\ H_2O + 2.5\ \square) \times 3$ a.p.f.u.

The content of F at the F(1) and F(2) sites equals 2 a.p.f.u., and the content of H₂O equals 1.5 a.p.f.u. (Table 7). The microprobe analysis gives F 4.89 a.p.f.u. (Table 1), and the monovalent anions sum to 43 a.p.f.u. (Table 7): 43 a.p.f.u. $\approx (OH)_{38.21}F_{4.89}$ a.p.f.u. The total anion content is therefore $O_{80}(OH,F)_{43}(H_2O)_{1.5}$ a.p.f.u. (Table 7) with a total charge 203^- .

Structure topology

The crystal structure of byzantievite is a framework of Ti-, Ba-, Ca-, Y-, REE-dominant polyhedra and SiO₄, PO₄ and BO₃ groups. Figure 1 presents a general view of the independent part of the structure, and the complete structure is generated by rhombohedral centring of the part shown in Fig. 1. For better understanding of the structure, we split the independent part (Fig. 1) into 16 sheets of polyhedra parallel

to (001). The B, H, J and P sheets consist of (Ti,Nb) polyhedra of medium size. The A and B–G sheets are composed of large Ba, (Ca,REE)-dominant polyhedra. We consider first the sheets of large polyhedra (Fig. 2).

A, C, D, E, F, G, I sheets of large polyhedra

The A sheet is composed of $A(1)$ polyhedra occupied by Ba and coordinated by 12 O atoms (Table 5). The $A(1)$ polyhedra connect *via* common vertices (Fig. 2a). The C sheet consists of trimers of [8]-coordinated $M(5)$ polyhedra and B(1) triangles (Fig. 2b). The $M(5)$ polyhedron is coordinated by: five O atoms; two anions, O(22) and O(26), which are O atoms and OH groups in the ratio 2:1 [O(22) and O(26) coordinate *T* sites occupied by P and Si with 63% occupancy, see *Anion sites* above]; and one F atom (Tables 5, 7). In a trimer, $M(5)$ polyhedra share common edges and a common vertex occupied by F. The $M(5)$ trimers share common vertices and edges with B(1) triangles to form a sheet. The D sheet is composed of [10]-coordinated $M(1)$ and $M(3)$ polyhedra and $T(1)$ tetrahedra (Fig. 2c). The $T(1)$ site is 63% occupied by P and Si in the ratio ~5:1, and its composition is $1.56\ P + 0.33\ Si + 1.11\ \square$ a.p.f.u. (Table 6). Where the $T(1)$ site is occupied by P or Si, the four ligands are O atoms; where the $T(1)$ site is vacant, ligands are OH groups (Tables 5, 7). All ligands of the $M(1)$ atom are ordered whereas the O(28) atom [which is bonded to $M(3)$] is disordered around the threefold axis. Thus we count O(28) as one ligand (Table 5), and Fig. 2c is drawn with the averaged coordinates of $O(28):O(28)_{av.} = 0,0,0.415$. The $M(1)$ and $M(3)$ polyhedra are coordinated by four O atoms [O(1), O(17) $\times 3$ and O(11) $\times 3$, O(28), respectively] and six additional anions, O(22) $\times 3$, O(23) $\times 3$ and O(26) $\times 3$, respectively, which are O atoms and OH groups in the ratio 2:1 [they coordinate the $T(1)$ site]. The $M(1)$ and $M(3)$ polyhedra are occupied by Ca, REE and Y. In the C sheet, the $M(1)$ and $M(3)$ polyhedra share common vertices and common edges with $T(1)$ tetrahedra.

The E sheet is formed by $M(2)$ polyhedra (mainly occupied by Ca and REE (Table 6), $T(1)$, Si(1) and Si(4) tetrahedra and B(3) triangles (Fig. 2d). $M(2)$ polyhedra share common vertices to form a trimer with a B(3) triangle in the centre. Each $M(2)$ polyhedron shares two edges with two $T(1)$ tetrahedra and a vertex with a third $T(1)$ tetrahedron (five common anions), a vertex with a B(3) triangle, and two vertices with Si(1) and

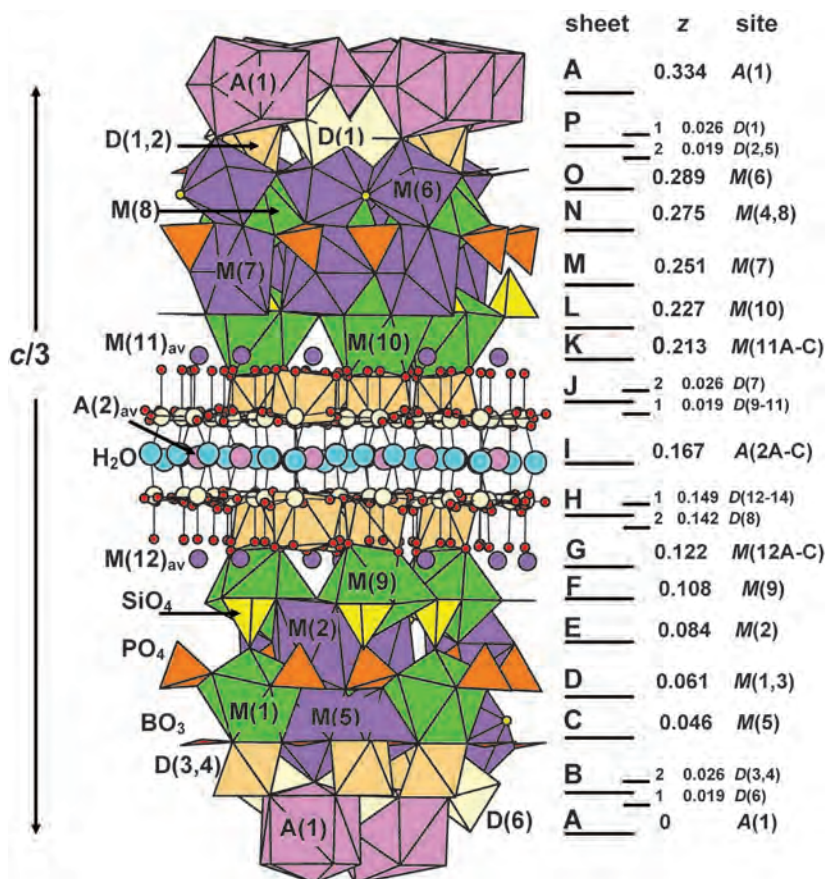


FIG. 1. General view of 1/3 of the crystal structure of byzantievite parallel to [001]. (BO_3) triangles, (SiO_4) and (PO_4) tetrahedra are red, yellow and orange respectively. Cation polyhedra are shown for sites with $>50\%$ occupancy: [12]-coordinated Ba polyhedra are pink, [10]- and [8]-coordinated M polyhedra are green and purple; Ti-dominant octahedra are dark yellow [D(2–5,7,8)] and pale yellow [D(1,6)]. Atoms at sites with $<50\%$ occupancy are shown as spheres: A(2A–C) – pink, D(9–14) – pale yellow, M(11A–C) and M(12A–C) – purple, triple sites A(2A–C), M(11A–C) and M(12A–C) are shown averaged as one sphere, A(2)_{av}, M(11)_{av} and M(12)_{av} where av = average. Fluorine and OH groups are shown as small yellow and red spheres. H_2O groups are shown as large turquoise spheres. The D(9–14)-anion bonds are shown as thin black lines. Sixteen (001) sheets of polyhedra within 1/3 of the c-cell parameter are indicated by black horizontal lines on the right of the figure. Each sheet is characterized by an approximate z coordinate and cation sites that occur in the sheet. Sheets of Ti-dominant octahedra (B, H, J and P) are divided into two subsheets, e.g. B₁ and B₂ where 1 and 2 correspond to pale yellow and dark yellow octahedra.

Si(4) tetrahedra. The M(2) polyhedron can be [8]- or [9]-coordinated depending on the occupancy of the O(28) site (with 33% occupancy by O atoms, see discussion above). In addition to O(28), there are eight other ligands of the M(2) atom: three O atoms, O(2,8,29), and five anions which are shared with T(1) tetrahedra; they are O atoms and OH groups in the ratio 2:1 (see discussion above) (Tables 5, 6, 7).

The F sheet is composed of M(9) polyhedra, Si(1) and Si(4) tetrahedra and B(3) triangles (Fig. 2e). The M(9) site is 55% occupied by (Ca, REE, Sr) and 45% occupied by □ (Table 6). The M(9) cation is coordinated by six O atoms; the seventh atom, O(20), also coordinates the T(1) site and can be either an O atom or an OH group in the ratio 2:1; three atoms, O(36,37,42), are O atoms of OH groups at 67% occupied anion sites

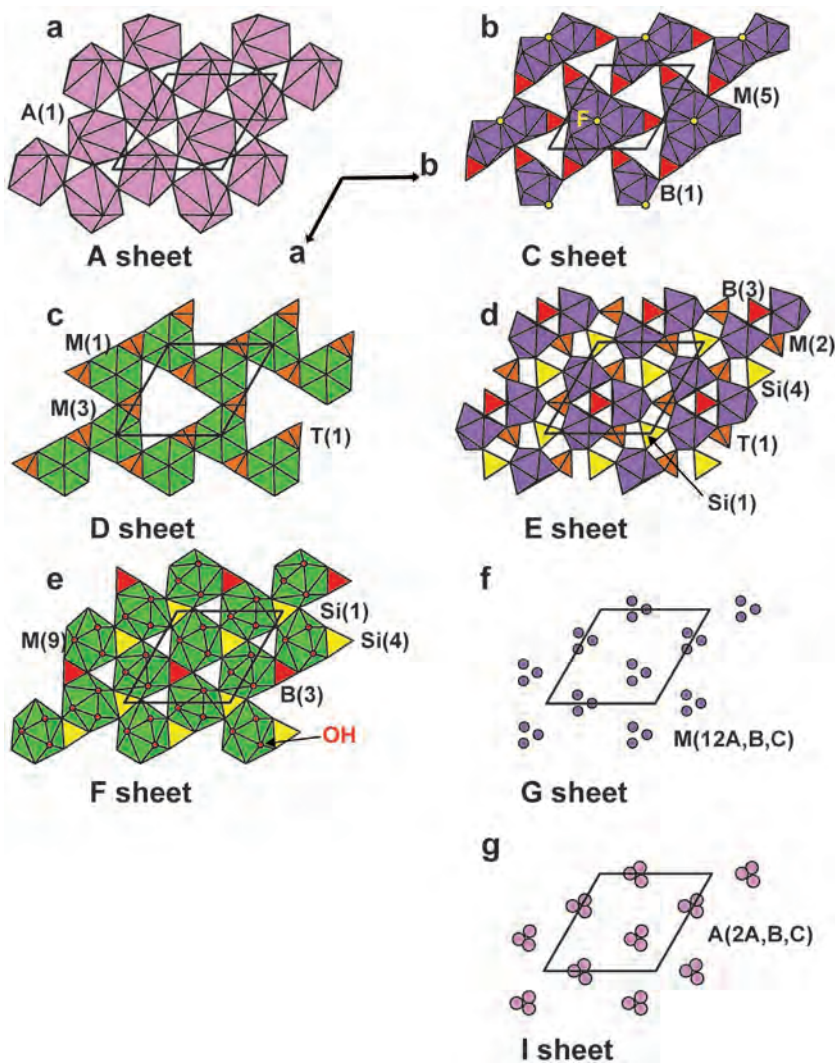


FIG. 2. Sheets of Ba- and Ca-, REE-, Y-dominant *A* and *M* polyhedra viewed down [001]: (a) the *A* sheet of $^{[12]}A(1)$ polyhedra; (b) the *C* sheet of $^{[8]}M(5)$ polyhedra and *B*(1) triangles; (c) the *D* sheet of $^{[10]}M(1,3)$ polyhedra and *T*(1) tetrahedra where $T = P > Si$; (d) the *E* sheet of $^{[8]}M(2)$ polyhedra, *B*(3) triangles, *Si*(1), *Si*(4) and *T*(1) tetrahedra; (e) the *F* sheet of $^{[10]}M(9)$ polyhedra, *B*(3) triangles and *Si*(1), *Si*(4) tetrahedra; (f) the *G* sheet of *M*(12*A–C*) atoms; and (g) the *I* sheet of *A*(2*A–C*) atoms. Legend as in Fig. 1.

which also coordinate the Ti-dominant *D*(8) site (Tables 5, 7). Therefore, the *M*(9) atom can be either: (i) [7]-coordinated by anions at fully-occupied sites, or (ii) [8–10]-coordinated depending on the occupancy of the O(36,37,42) sites, all of which occur to one side of the *M*(9) cation (Fig. 2e). Each *M*(9) polyhedron shares a vertex with each of six *M*(9) neighbours, and one

and two edges with a *B*(3) triangle and *Si*(1,4) tetrahedra respectively.

Figure 2f,g shows the *G* sheet of *M*(12*A–C*) atoms and the *I* sheet of *A*(2*A–C*) atoms. The *M*(12*A–C*) and *A*(2*A–C*) sites are occupied by REE at 17% and Ba at 22% respectively (Table 6). We were unable to locate all anions coordinating the *M*(12) and *A*(2) atoms (Table 5).

There is a similarity between the A, D and F sheets: in a sheet, each polyhedron shares vertices with six neighbouring polyhedra and all polyhedra lie at the nodes of a 3^6 net (Fig. 2*a,c,e*). The G and I sheets obey the 3^6 -net pattern. In the C and E sheets, trimers of $M(5)$ and $M(2)$ polyhedra occur at the nodes of a 3^6 net. Sheets C and O, D and N, E and M, F and L, G and K are related by a pseudo-mirror plane m_z at $z \sim 0.167$ (Fig. 1); sheets K, L, M, N and O are similar to sheets G, F, E, D and C, respectively.

B and H sheets of medium-sized polyhedra

Titanium-dominant $D(3,4,6)$ octahedra and B(1) triangles share common vertices to form the B sheet (Fig. 3*a*). The topology of the B sheet of fully occupied sites is crucial to understanding the topologies of the (Ti,Nb) fragments in the disordered part of the structure of byzantievite. For a better understanding of the topology of the B sheet, we divide it into two subsheets, B_1 and B_2 . The B_2 subsheet is an array of isolated $D(3,4)$ octahedra connected through B(1) triangles

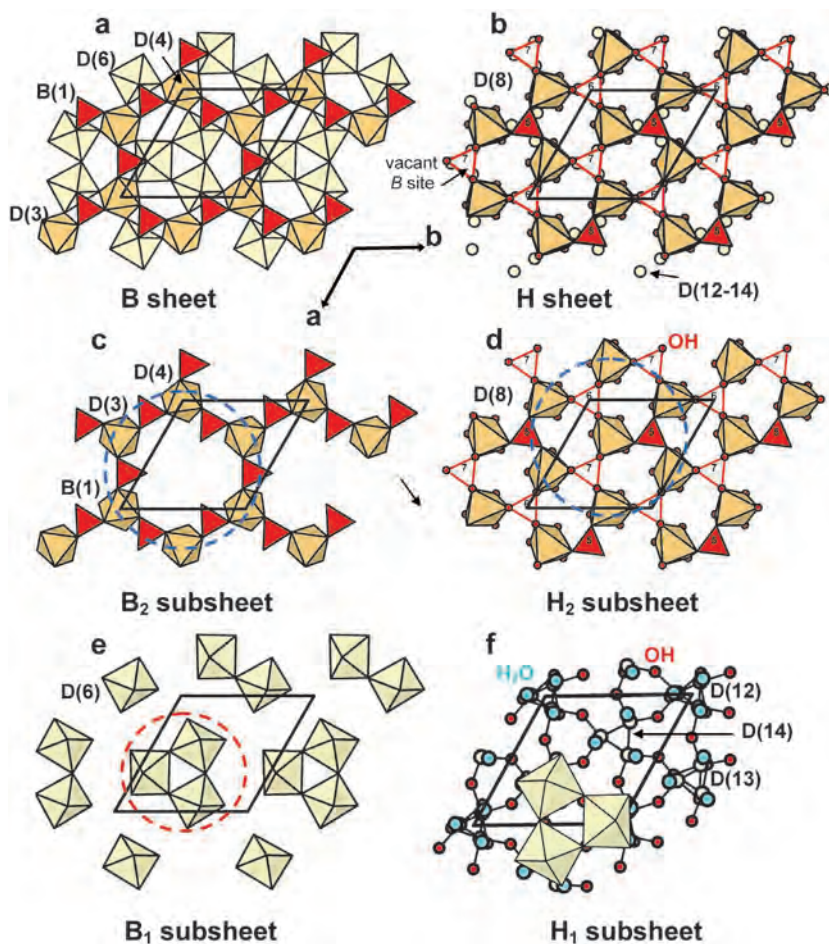


FIG. 3. Sheets of (Ti,Nb) octahedra viewed down [001]: (a) the B sheet of $D(6)$ (pale yellow) and $D(3,4)$ (dark yellow) octahedra and B(1) triangles; (b) the H sheet of $D(12-14)$ atoms (pale yellow) and $D(8)$ (dark yellow) octahedra and B(5-7) triangles; (c) the B_2 subsheet of $D(3,4)$ octahedra and B(1) triangles; (d) the H_2 subsheet of $D(8)$ octahedra and B(5,6,7) triangles; (e) the B_1 subsheet of $D(6)$ octahedra; and (f) the H_1 subsheet of $D(12-14)$ atoms, OH and H_2O groups. Vacant B sites with the three closest anions are shown as white triangles with red edges, a ring of D octahedra and B triangles is shown by blue dashed line in (c) and (d); a trimer of octahedra is encircled by a red dashed line in (e) and is projected onto the H_1 sheet in (f). Legend as in Fig. 1.

(Fig. 3c) and occurs at $z \sim 0.026$. The ring of $D(3,4)$ octahedra and B(1) triangles is shown by a blue dashed line in Fig. 3c. The B_1 subsheet is an array of trimers of $D(6)$ octahedra and occurs at $z \sim 0.019$ (Fig. 3e). In the B sheet, the $D(3)$ and $D(4)$ octahedra and trimers of $D(6)$ octahedra lie at the nodes of a 3^6 net (Fig. 3a,c,e).

Consider the H sheet. Figure 3b shows the arrangement of Ti dominant $D(8)$ octahedra, B(5,6,7) triangles and $D(12-14)$ atoms in the H sheet. The $D(8)$ and $D(12-14)$ sites are occupied by Ti (+ Nb) at 67% (group 2) and 17%, respectively, and the B(5,6,7) sites are 17% occupied by B (Table 6). Consider the H_1 and H_2 subsheets; the H_2 subsheet is an array of isolated $D(8)$ octahedra and B(5,6,7) triangles (Fig. 3d). White and red triangles indicate vacant and fully occupied B sites. Where a B site is occupied by B, its common vertex with a $D(8)$ octahedron is an O atom; where a B site is vacant, the former common vertex with a $D(8)$ octahedron is an OH group. Depending on the occupancy of the adjacent B sites, a $D(8)$ octahedron can have one of the following forms: $D(OH)_6$, $DO(OH)_5$, $DO_2(OH)_4$ and $DO_3(OH)_3$. Therefore, in the H_2 subsheet, $D(8)$ octahedra connect either through B triangles or hydrogen bonds. Comparison of B_2 and H_2 subsheets reveals common features, one of them being a ring of isolated D octahedra and B triangles. In the B_2 subsheet, the centre of the ring is empty, whereas in the H_2 subsheet, there is an octahedron at the centre of the ring. As the $D(8)$ sites are 67% occupied by Ti (group 2), the topology of the D ring in the H_2 subsheet can be identical to that in the B_2 subsheet. In the H_1 subsheet, there are (Ti,Nb) atoms at the $D(12-14)$ sites with occupancies of 17%. The $D(12-14)$ sites are each coordinated by five OH groups (17 and 33% occupancy, see Table 7 and discussion above) and an H_2O group (17% occupancy). Each of the $D(12)$, $D(13)$ and $D(14)$ sites is disordered around threefold axis and they are each separated by short distances (~ 1.5 Å) from two other equivalent sites, e.g. $D(12)-D(12)' = 1.554 \times 2$ Å (Fig. 3f, Table 5). Taking into account one of three disordered equivalent sites, we were able to identify a trimer of octahedra identical to that in the B_1 subsheet (compare Fig. 3f and 3e). We conclude that both sheets of Ti octahedra and B triangles, B and H, have similar topologies but differ in the degree of order of their constituent cations and anions: the B sheet is fully ordered and all constituent sites are 100% occupied; the H

sheet is disordered and the constituent sites are only partly occupied (67–17%). The B and P, and H and J sheets are related by a pseudo-mirror plane m_z at $z \sim 0.167$ (Fig. 1) and hence the P and J sheets are similar to the B and H sheets.

Short-range order

We have divided the 50 cation sites in the crystal structure of byzantievite (Table 6) into three groups, with 100%, 67% and 17% occupancy (see above). Group 1 (100%) comprises the following sites: Si(1–4), B(1–4), A(1), $D(1-6)$ and $M(1-8)$; group 2 (67%) comprises the $M(9,10)$, $T(1,2)$ and $D(7,8)$ sites; and group 3 (17%) consists of the B(5–10), $D(9-14)$; $M(11A-C)$, $M(12A-C)$ and $A(2A-C)$ sites. Figure 4a shows the component of the structure that consists of polyhedra around 23 cation sites with 100% occupancy. These polyhedra constitute the long-range ordered component of the structure, and the empty space in Fig. 4a corresponds to the disordered part of the structure. We do not know exactly what the topology of the disordered part of the average long-range-ordered structure is. However, we know that: (1) there are two groups of partly occupied cations sites, with 67 and 17% occupancy; (2) there are two groups of anions, O(32–43) and O(44–64), with 67 and (17, 33)% occupancy; and (3) both groups – cations and anions – occur at short distances from each other and are mutually exclusive (Table 5). Hence, we propose two short-range-ordered (SRO) arrangements, with 67% and 17% occupancy of cation (and anion) sites, for the disordered part of the structure.

Consider first the sites with 67% occupancy (group 2) (Fig. 4b). Here, the disordered component consists of the F and L sheets of $M(9)$ and $M(10)$ polyhedra occupied by Ca, REE and Sr at $\sim 55\%$ (group 2) (cf. Fig. 2e), the J_2 and H_2 subsheets of Ti-dominant $D(7,8)$ octahedra occupied at 69% (group 2) (cf. Fig. 3d), and the I sheet of Ba atoms at the $A(2A-C)$ sites (cf. Fig. 2g). Although each of $A(2A-C)$ sites has a 22% occupancy (group 3), each $A(2)$ trimer sums to $\sim 66\%$ occupancy. We consider the $A(2)$ cations as part of our 67% SRO model as they share anions with the $D(7,8)$ atoms (see Table 5). The P-dominant $T(1)$ and $T(2)$ tetrahedra link pairs of the (D and E) and (N and M) sheets composed of large polyhedra occupied by Ca, REE and Y.

Consider next the sites with 17% occupancy (group 3) (Fig. 4c). In this case, the disordered

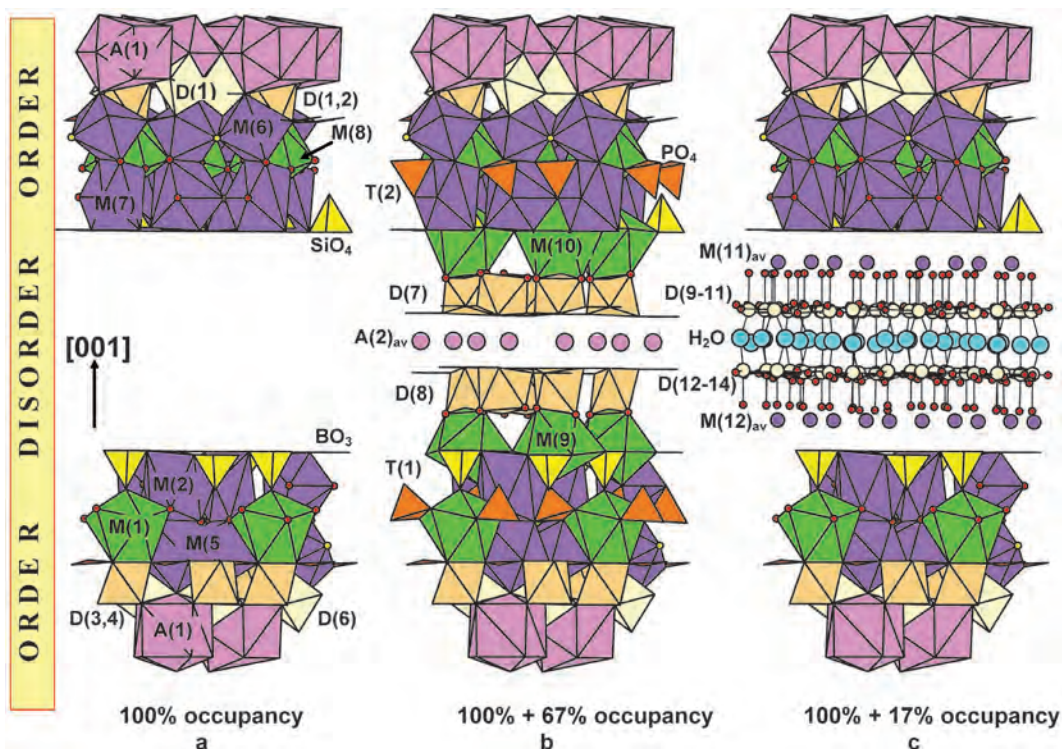


FIG. 4. Short-range order in the crystal structure of byzantievite: (a) the ordered component of the crystal structure where cation sites are 100% occupied; (b–c) short-range-order models for the disordered components of the structure, (b) sites with 100% + 67% occupancy and (c) sites with 100% and 17% occupancy. Triple sites $A(2A-C)$, $M(11A-C)$ and $M(12A-C)$ are shown averaged as one sphere, $A(2)_{av}$, $M(11)_{av}$, and $M(12)_{av}$. Legend as in Fig. 1.

component of the structure is composed of the K and J sheets of $M(11A-C)$ and $M(12A-C)$ sites occupied by REE (cf. Fig. 2f) and the J_1 and H_1 subsheets of Ti-dominant $D(9-11)$ and $D(12-14)$ trimers (cf. Fig. 3f). Titanium trimers of different subsheets link through H₂O groups. The $T(1)$ and $T(2)$ sites are vacant and the O(19–26) sites are occupied by OH groups which provide hydrogen bonding between polyhedra occupied by Ca, REE and Y in pairs of the (D and E) and (N and M) sheets.

For the disordered part of the structure, we have considered SRO arrangements with 67% and 17% occupied cation sites. These two arrangements cover $67 + 17 = 84\%$ of the disordered part of the structure; what occurs in the 16% left unoccupied? We suggest that the 67% and 17% SRO models are not mutually exclusive but co-exist together as cation clusters connected by hydrogen bonds.

Structure topology: summary

The structure of byzantievite is extremely complex. It is an intercalation of three components, one fully ordered with full occupancy of cation sites, and two partly ordered with cation-site occupancies of 67% and 17% respectively. For the domain with 17% occupancy of the cation sites, we were unable to locate all anions directly from difference-Fourier maps and we consider this component only as a partial model of the structure. However, we tested the structure with bond-valence calculations, and bond-valence sums at all cations and anions are in reasonable accord with calculated total aggregate charges (Tables 6, 7).

The major constituent of the disordered part of the structure is an array of (Ti,Nb) octahedra. In spite of the profound disorder of that array, we can see common features in the topology of the B (ordered component) and H (disordered components) sheets of Ti-dominant octahedra (Fig. 3).

Out of 16 sheets of polyhedra in a translationally independent part of the structure (Fig. 1), seven sheets, B, C, D, E, F, G are related to another seven sheets, P, P, N, M, L, K, J, by a pseudo-mirror plane m_z which coincides with the I sheet at $z \sim 1/6$. An analogous pseudo-mirror plane m_z occurs in the A sheet at $z \sim 0$. Each plane exerts its pseudo-symmetry operation within a translationally independent part of the structure (1/3): e.g. the Ba-dominant A sheets at $z \sim 0$ and $z \sim 1/3$ are not related by a mirror plane at $z \sim 1/6$. Mirror planes are not compatible with rhombohedral symmetry, but the presence of pseudo-mirror planes shows that the structure lacks an inversion centre.

Chemical formula

We combine the cation and anion parts into the structural formula $(\text{Ba}_{4.98}\square_{7.02})\{[(\text{Ca}_{8.99}\text{Sr}_{0.96}\text{Fe}_{0.42}^{2+}\text{Na}_{0.20})_{\Sigma 10.57}(\text{REE}_{7.49}\text{Th}_{0.39}\text{U}_{0.17}^{4+})_{\Sigma 8.05}\text{Y}_{3.53}]_{\Sigma 22.15}\square_{17.85}\}[(\text{Ti}_{11.86}\text{Nb}_{5.30})_{\Sigma 17.16}\square_{16.84}]\text{Si}_4(\text{P}_{3.12}\text{Si}_{0.66}\square_{2.22})(\text{B}_9\square_5)\text{O}_{80}(\text{OH},\text{F})_{43}(\text{H}_2\text{O})_{1.5} = [(\text{Ca}_{8.99}\text{Sr}_{0.96}\text{Fe}_{0.42}^{2+}\text{Na}_{0.20})(\text{REE}_{7.49}\text{Y}_{3.53}\text{Th}_{0.39}\text{U}_{0.17}^{4+})\square_{17.85}][(\text{Ti}_{11.86}\text{Nb}_{5.30})\square_{16.84}](\text{SiO}_4)_4[(\text{PO}_4)_{3.12}(\text{SiO}_4)_{0.66}\square_{2.22}][(\text{BO}_3)_9\square_5]\text{O}_{21.88}(\text{OH},\text{F})_{43}(\text{H}_2\text{O})_{1.5}$. This formula has an excess negative charge of 1.6, i.e. 203 (anions)–201.4 (cations). This excess charge is due mainly to the difference in content of Ti as obtained from the chemical analysis ($\text{Ti}_{12.31}$) and the structure refinement ($\text{Ti}_{11.86}$), i.e. $\text{Ti}_{0.45}$ with a charge of 1.8^+ . It is very difficult to estimate the accuracy of the structure refinement for such a complex structure characterized by such profound disorder. The measured density, $4.10(3) \text{ g cm}^{-3}$ (Pautov *et al.*, 2010) is compatible with the model of partial occupancies presented here (calculated density = 4.151 g cm^{-3}). We write a simplified formula by grouping the cations as indicated by their occupancies of sites in the structure and we adjust Ti + Nb to be 18 a.p.f.u. In accord with the chemical analysis; we omit vacancies in this process as the resulting formula then becomes too complicated to be informative: $\text{Ba}_5(\text{Ca},\text{REE},\text{Y})_{22}(\text{Ti},\text{Nb})_{18}(\text{SiO}_4)_4[(\text{PO}_4),(\text{SiO}_4)]_4(\text{BO}_3)_9\text{O}_{21}[(\text{OH},\text{F})_{43}(\text{H}_2\text{O})_{1.5}, Z = 3$.

Minerals with three different oxyanions

The crystal structure of byzantievite strongly violates Pauling's (1929) fifth rule: "...The number of essentially different kinds of constituents in a crystal tends to be small. The repeating

units will tend to be identical because each atom in the structure is most stable in a specific environment. There may be two or three types of polyhedra, such as tetrahedra or octahedra, but there will not be many different types...". Only three other structurally characterized minerals contain $n \geq 3$ oxyanions in their end-member formulae. They are abenakiite-(Ce), $\text{Na}_{26}\text{REE}_6(\text{Si}_6\text{O}_{18})(\text{PO}_4)_6(\text{CO}_3)_6(\text{S}^{4+}\text{O}_2)$, $n = 4$ (McDonald *et al.*, 1994), britvinite, $[\text{Pb}_7(\text{OH})_3(\text{BO}_3)_2(\text{CO}_3)] [\text{Mg}_{4.5}(\text{OH})_3(\text{Si}_5\text{O}_{14})]$, $n = 3$ (Yakubovich *et al.*, 2008) and devitoite (astrophyllite group), $[\text{Ba}_6(\text{PO}_4)_2(\text{CO}_3)][\text{Fe}_2^{3+}\text{Fe}_7^{2+}(\text{Si}_4\text{O}_{12})_2\text{O}_2(\text{OH})_4]$, $n = 3$ (Kampf *et al.*, 2010). All minerals are characterized by a certain degree of disorder, including one or two of the $n \geq 3$ oxyanions.

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